TITANIUM, ZIRCONIUM AND HAFNIUM

ANNUAL SURVEY COVERING THE YEAR 1976

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This survey follows the basic organizational scheme used in previous years, with complexes classified according to ligand type. Complexes with more than one class of ligand will be found under the feature of primary interest. A section on synthetic and catalytic applications has been added; most of the coverage will be brief since this topic is surveyed separately. The abbreviations Cp (for η^5-cyclopentadienyl) and Cp' (for any ring-substituted cyclopentadienyl group) have been used throughout.

A review emphasizing preparative details for selected group IVa organometallic compounds has appeared in the Houben-Weyl series (1).

CARBONYL AND DINITROGEN COMPLEXES

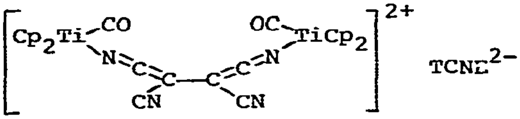
The previously unknown Zr (and Hf) analog of $Cp_2Ti(CO)_2$ has been independently prepared by three methods: i) reduction of Cp_2MCl_2 with Na(Hg) under CO (1 atm) (2); ii) reduction of Cp_2MCl_2 with Li under CO (200 atm) (3); and iii) treatment of Cp_2MBH_4 with Et_3N under CO (1 atm) (4). Yields obtained were:

Method	M = Ti	Zr	Hf
i	80%	9%	30%
ii	(not reported)	80%	2%
iii	80%	15%	(not reported)

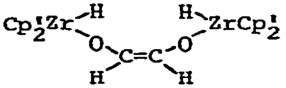
Titanium, zirconium and hafnium, Annual Survey covering the year 1975 see J.Organometal.Chem., Vol. 126(1977)361-382.

In all cases the NMR and IR spectra agreed and were quite similar from one metal to the next, with the CO stretching frequencies decreasing in the order Ti > Zr > Hf. The Zr and Hf compounds are much less effective catalysts for hydrogenation of diphenylacetylene than the Ti compound (2).

Reaction of $Cp_2Ti(CO)_2$ with TCNE gave an air-sensitive, diamagnetic product analyzing as $Cp_2Ti(CO)(TCNE)$, with ν_{CO} = 2055 cm^{-1}. From the IR and solubility this was tentatively assigned the dimeric, ionic structure:



which, if correct, would be the first isolated Ti(IV) (d^0) carbonyl (5). NMR evidence for a Zr(IV) carbonyl has been cited: exposure of a solution of $(C_5Me_5)_2ZrH_2$ to CO at -80° gives a new complex identified as $Cp'_2ZrH_2(CO)$ by the observation of ^{13}C-H coupling when ^{13}CO was used; unfortunately no IR could be obtained. This important paper also reports the first example of reduction of coordinated CO by H_2: $Cp'_2Zr(CO)_2$ (prepared by carbonylation of an N_2 complex; vide infra) reacts with H_2 under heating or photolysis to give the methoxy complex $Cp'_2ZrH(OCH_3)$. A different product is obtained on allowing $Cp'_2ZrH_2(CO)$ to warm: carbon-carbon bond formation takes place and a dimer with an enediol bridging ligand is produced (6):

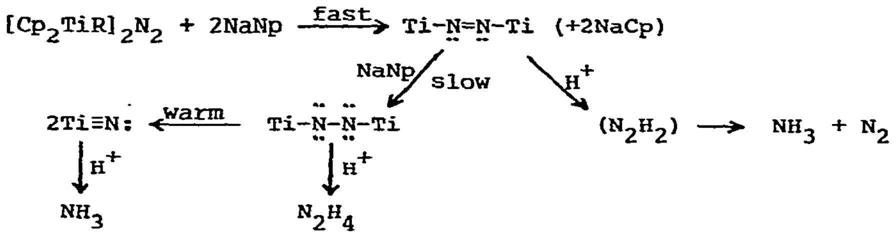


Although this system is not catalytic, these CO reductions may provide models for the as yet unknown homogeneous analogs of methanol synthesis and the Fischer-Tropsch reaction.

Crystal structures of the dinitrogen complexes $[(C_5Me_5)_2Ti]_2N_2$ and $[(C_5Me_5)_2Zr(N_2)]_2N_2$ have been reported. The Ti complex contains trigonal (Cp'_2TiX) groups, not previously observed, with a linear ("end-on") Ti-N=N-Ti bridge; previous suggestions of possible "side-on" bridging N_2 or monomeric Cp'_2TiN_2 appear to be incorrect (7). The zirconium complex allows a comparison between terminal and bridging N_2 groups in the same compound: the bridging N_2 has the longer N-N distance (1.18 vs. 1.115 Å) and shorter Zr-N distances. The bridging N_2 stretching frequency is exceptionally low, 1578 cm^{-1}; MO arguments are proposed to account for these results (8). Surprisingly, although increased bond length and decreased stretching frequency have usually been assumed to be associated with increased reactivity of coordinated N_2, a labelling study shows that in the previously reported protonolysis of this dimer, the hydrazine produced comes equally from terminal and bridging N_2. An intermediate was proposed in which the bridging and one terminal N_2 have become equivalent, such as $Cp'_2Zr(N_2H)_2$. In agreement, it was found that careful carbonylation of the dimer gives $[Cp'_2Zr(CO)]_2N_2$ (further carbonylation leads to $Cp'_2Zr(CO)_2$), which on protonolysis gives no reduced form of N_2, indicating both bridging and terminal N_2 is required (9).

Studies on the mechanism of N_2 reduction in Ti(III) complexes $[Cp_2TiR]_2N_2$ (R = aryl or benzyl) have been reported. Thermal decomposition gives, after hydrolysis, mostly N_2, but up to 10% NH_3 per Ti (and traces of N_2H_4) were formed; no organic amines such as RNH_2 were detected. Reduction with sodium naphthalenide (NaNp) gives virtually quantitative reduction to NH_3:

other reducing agents such as LiBu or i-PrMgCl were less effective (10). Complete reduction required 2 moles of NaNp/Ti; under these conditions NaCp was formed (by NMR) and hydrolysis with HCl gave $CpTiCl_3$ as the major product; larger excesses of NaNp gave more Cp cleavage. Reduction at low temperatures gave initially NH_3, but mostly N_2H_4 was obtained for longer reaction times, while warming before hydrolysis gave mostly NH_3 again. The following mechanism was proposed (11):



A form of "titanocene", $Cp_3(C_5H_4)Ti_2$ (vide infra) reacts with N_2 to give a complex of stoichiometry $[Cp_3(C_5H_4)Ti_2]_2N_2$. Reduction of the latter with NaNp gives 1.4 moles NH_3 per N_2, while reaction with H_2 results only in the displacement of N_2 (12).

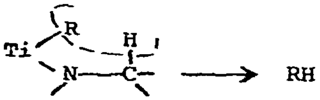
ALKYL AND ARYL COMPLEXES

Two general reviews on transition metal alkyls contain substantial material of relevance to this group: one deals specifically with binary ("homoleptic") metal alkyls, MR_n, emphasizing trends in stability and decomposition mechanisms (13). The other is an extensive review of alkyl and aryl complexes of the "early" transition metals, IVa-VIIa (14).

Excess $TiCl_4$ reacts with $(Me_3SiCH_2)_3Al{\cdot}OEt_2$ to give $(Me_3SiCH_2)TiCl_3$, previously obtained using the Grignard reagent; this compound catalyzes butadiene polymerization (15). A variety of transition metal halides, including $TiCl_4$, were found to cause decomposition of silanes Me_3SiR; only from

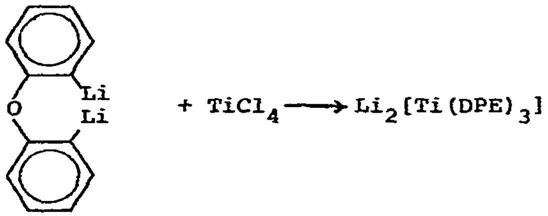
$TiCl_4$ and Me_3SiPh was an R-Ti compound obtained (17). Preparative details for $TiMeCl_3$ and $TiMeBr_3$ have been reported (18).

A number of mixed alkyl-dialkylamido complexes $R_nTi(NR'_2)_{4-n}$ have been prepared (R = CH_3, CH_2Ph, CH_2SiMe_3) for a study of thermal decomposition mechanisms. Although the bulkier R'_2N ligands tend to stabilize compounds, they also provide a source of H in an alternate mechanism for RH elimination:



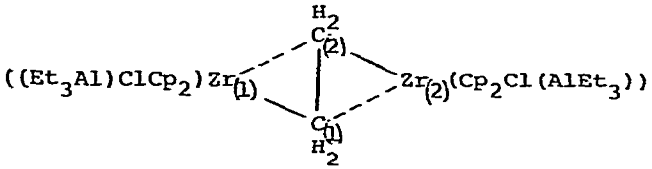
The net result is that the stability order is: $R_4Ti>R_3Ti(NR'_2)$-$R_2Ti(NR'_2)_2<RTi(NR'_2)_3<Ti(NR'_2)_4$ (19). A "ruthenocenyl" compound, $Ru(\eta^5-C_5H_4Ti(NEt_2)_3)_2$, was prepared from 1,1'dilithioruthenocene and $TiBr(NEt_2)_3$, and found to be somewhat more stable than the known ferrocene analog (20).

$Zr(C_6F_5)_4$ was prepared from $ZrCl_4$ and LiC_6F_5 and isolated as the crystalline etherate; it is thermally stable to >100° (21). A chelated aryl complex was made from dilithiated diphenyl ether (DPE) (22):



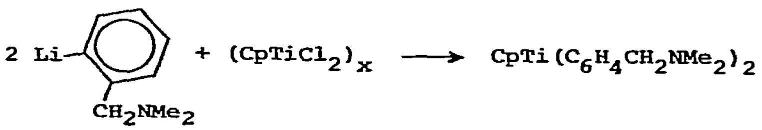
The exchange reaction between R_3Al and R'_4Ti has been studied by NMR for R,R' = CH_3 and CH_2Ph; an intermediate of form $[R'_3Ti]^+[R'R_3Al]^-$ seems to be involved but mechanistic details are unclear (23). The benzyl complexes $M(CH_2Ph)_4$ (M = Ti, Zr, Hf) are hydrogenated in the presence of $Me_2PCH_2CH_2PMe_2$ (dmpe) to give $(dmpe)_2MH_3$ (24).

A number of crystal structures of cyclopentadienylmetal alkyls have recently been published. $Cp_2Ti(2,6\text{-}C_6H_3Me_2)$ is unusually thermally stable, a fact attributed to the steric effects of the two ortho methyl groups. The aryl group is found to lie perpendicular to the plane defined by the metal and ring centers, and cannot move significantly without introducing strongly unfavorable interactions between a methyl group and a Cp ring (25). Both $Cp_2Hf(CH_3)_2$ and its air-oxidation product, $(Cp_2Hf(CH_3))_2O$, have generally predictable structural features, although in the dimethyl complex the two Cp-Hf distances are significantly different, for no obvious reason (26). Structures of several products from the $Cp_2ZrCl_2\text{-}AlEt_3$ system (see last year's survey) have been reported, including $(Cp_2ZrCl(AlEt_3))_2C_2H_4$ and $[Cp_2ZrCH_2CH(AlEt_2)_2]^+Cp^-$. In both cases the zirconium-carbon bonding appears to be intermediate between a σ-ethyl and a π-ethylene type of complex; e.g., for the first:

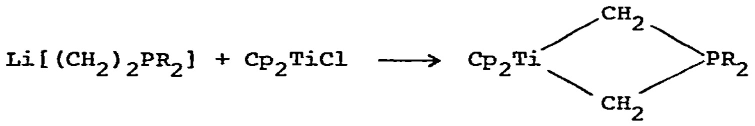


with bond lengths $Zr_{(1)}\text{-}C_{(1)} = 2.36$ Å, $Zr_{(1)}\text{-}C_2 = 2.49$ Å, and $\angle Zr_{(1)}\text{-}C_{(1)}\text{-}C_{(2)} = 76^\circ$. The π-bonding view would make this a bridged $(\eta^2)_2$-C_2H_4 species, a rather novel structural feature. In the second complex one Cp is not bonded to Zr but appears to be a free anion in the lattice (27).

The following reaction affords a chelated Ti(III) aryl complex:



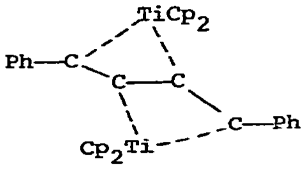
the magnetic moment is 1.7 B.M.; the crystal structure shows both ligands bidentate. Although this compound has formally 15 electrons, it does not add ligands such as pyridine or PMe_3; CO_2 adds at 85° to give a substituted benzoate derivative (28). A different type of Ti(III) chelate was prepared from anionic phosphorus ylides:



EPR data are reported; these compounds can transfer methylene to cyclohexanone (29).

The metallocycles $Cp_2M(C_4Ph_4)$ (M = Ti, Hf) were prepared by photolyzing $Cp_2M(CH_3)_2$ in the presence of diphenylacetylene. In both cases, the M-C σ-bonds are considerably shorter than the metal-Cp carbon distances, a feature which has been observed in other early transition metal complexes containing both types of ligands. In contrast, similar complexes of later transition metals generally have longer M-C σ-bonds. This difference was attributed to trends in relative energies of the metal orbitals involved in bonding: d orbitals, which are most important for M-Cp bonding, are higher in energy than s and p orbitals at the beginning of each transition series but drop more sharply on moving from left to right across the series (30).

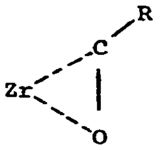
Cp_2TiCl reacts with Na[C≡CPh] to give a diamagnetic product, inconsistent with the anticipated Ti(III) phenylacetylide; a crystal structure determination shows that coupling of two acetylides has occurred to give:



which can be considered either as a Ti(II) π-complex of PhC≡C-C≡CPh or as an alkenyltitanium(IV) complex; the geometry of the ligand, as indicated above, appears more in agreement with the latter formulation, although the geometry about Ti does not resemble Cp_2TiR_2 species. The same complex was obtained by reducing Cp_2TiCl with Na in the presence of PhC≡C-C≡CPh. A purple intermediate with an IR peak at 2045 cm^{-1} can be observed in the first reaction but not in the second; this is thought to be a Ti-C≡CPh species (31). A thesis which includes these studies has been abstracted (32).

A full paper has appeared on the chemistry of $Cp_2Ti(CH_2)_4$, prepared from Cp_2TiCl_2 and 1,4-dilithiobutane. This compound is not very stable ($\tau_{1/2}$~30 min at 0°) but is far more so than the non-chelate analog, $Cp_2TiBu^n_2$; this difference is attributed to inhibition of the β-hydride elimination path for the metallocycle by conformational restriction. Thermal decomposition of the metallocycle gives a mixture of ethylene and 1-butene, showing that C-C cleavage can compete with β-hydride elimination. The reverse of this process was also observed: addition of ethylene to $(Cp_2Ti)_2N_2$ at -30° gave a complex which showed identical reactivity to the metallocycle; e.g., reaction with CO to give cyclopentanone. Coupling of other olefins to substituted cyclopentanones by this method was demonstrated. The zirconium analogs were briefly examined and appear to behave similarly (33).

The zirconium alkyls Cp_2ZrR_2 (R = CH_3, CH_2Ph) had been previously thought to be unreactive towards CO since the expected IR peak for the acyls was not observed. It is now reported that these compounds in fact do absorb (reversibly) one mole of CO to give $Cp_2Zr(RCO)R$ with a π-bonded acyl group:



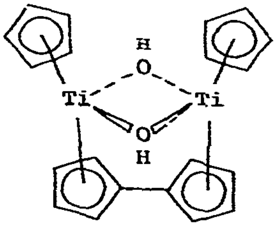
as shown by the crystal structure of the methyl compound; the CO stretch had been missed because it appears at very low frequency, 1540 cm^{-1} (34). The stability of this alkyl-acyl complex towards reductive elimination is also notable; presumably it is due to the unusual coordination of the acyl group. Insertion reactions of some titanium alkyls have been studied. Cp_2TiMe_2 reacts with $C_6H_{11}NC$ to give $Cp_2TiMe(C(Me)=NC_6H_{11})$ while $CpTiMe_3$ gives products resulting from multiple insertions. $CpTiMe_3$ was also reacted with NO, to give $CpTiMe(ON(Me)NO)_2$; with SO_2, to give $CpTiMe_2(O_2SMe)$; and with CO, to give an uncharacterized product with Ti-O bonds. $CpTiMe_3$ does not react with bipyridyl or o-$C_6H_4(AsMe_2)_2$ (diars), in contrast to $CpTiCl_3$ which gave isolable adducts with both bidentate ligands (35). The stereochemically labelled zirconium alkyl, $Cp_2ZrCl(CHDCHDCMe_3)$, is cleaved to $Me_3CCHDCHDBr$ by $CuBr_2$ with complete loss of stereospecificity, suggesting a free radical intermediate (36).

Studies continue on the mechanism of thermal decomposition of metal alkyls. An automated system was used to examine products from $Cp_2M(CH_3)_2$, M = Ti, Zr, Hf. In all cases the major product was CH_4, with the additional H coming from both other methyl groups and the Cp rings; e.g., $Cp_2Ti(CD_3)_2$ gave CD_3H and CD_4 in a 3:1 ratio. C_5H_6 was a minor product; also, for Ti, which showed autocatalytic behavior in decomposing rapidly at 120-125°, C_2H_4 and traces of C_2H_6 and $C_5H_5CH_3$ were observed. It has been thought that formation of ethylene in such reactions proceeds via intermediates such as $Ti=CH_2$, formed by α-hydride eliminaation; however, from $Cp_2Ti(CD_3)_2$ only C_2H_4 was obtained, indicating that the ethylene is coming fom degradation of the Cp rings, not the methyl groups (37). This result is rather surprising, considering the relatively low temperature at which decomposition occurs. A similar study on Cp_2TiR_2 (R = CH_3,

CH_2Ph, Ph) as well as the non-alkyls Cp_2TiCl_2 and "Cp_2Ti" (from hydrogenolysis of $Cp_2Ti(CH_3)_2$) gives analogous results: for alkyl compounds, RH is the major product; in all cases, hydrocarbons such as CH_4 and C_2H_6 were also detected, and these must come from the Cp rings for non-alkyl compounds (38). An investigation of the thermolysis of $Cp_2Ti(CH_3)_2$ in solution is in basic agreement with the above, but evidence was found in some cases for a free radical pathway contribution; e.g., in ether-d_{10} a significant amount of CH_3D was formed, while in CCl_4 traces of CH_3Cl were observed. Again small amounts of ethane were detected, and it was noted that ring-deuterated samples gave highly deuterated ethane, interpreted as resulting from H-D exchange between methyls and Cp's, followed by reductive elimination (39). In view of the above results, it is more likely that the ethane is coming directly from ring degradation.

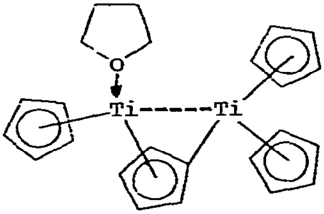
CYCLOPENTADIENYL COMPLEXES

Two important structural studies shed some light on the nature of low-valent Cp_2Ti-systems--so-called titanocene. The "stable" form of titanocene had previously been assigned a fulvalene-bridged structure, $(CpTiH)_2(C_{10}H_8)$, based on ^{13}C NMR and other studies, but a crystal structure could not be obtained for this species. It is now reported that the compound reacts rapidly with water to give a hydroxo-bridged complex, $(CpTi(OH))_2(C_{10}H_8)$, for which an X-ray crystallographic study confirms the fulvalene-bridged structure:



While the Ti-Ti distance is rather long (3.195 Å), the compound is only weakly paramagnetic (0.84 B.M.), indicating some kind of interaction between spins; the question of whether a Ti-Ti bond can be said to be present was left open (40).

The first reduced Cp_2Ti species for which a crystal structure has been determined was obtained by reducing Cp_2TiCl_2 with potassium naphthalenide in THF at -80°. It is perhaps ironic that the resulting black product appears not to be an isomer of Cp_2Ti; instead, it has the formula $(C_5H_5)_3(C_5H_4)Ti_2 \cdot 2THF$. The structure shows a single $(\eta^5,\eta^1\text{-}C_5H_4)$ group bridging a (formally) Ti(II) and Ti(III) center, with one THF coordinated to Ti(II) and the other a solvent of crystallization:



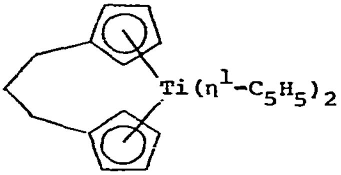
A solvent-free product was also obtained and appears, from spectral data, to have the same basic structural features. No evidence for a Ti-bonded hydride (which would make the species isomeric to Cp_2Ti) could be seen in the structure or chemical reactivity, although this result was not considered entirely conclusive. The most notable feature of the structure is the large, unhindered region from which potential ligands can approach the Ti centers, resulting from the presence of only one bridging group. The Ti-Ti distance is 3.336 Å, even longer than the above hydroxo complex. It is not yet clear what is the relationship between this structure and the various other forms which have been reported as titanocene (41).

On heating the above compound for several days at 100°, it is transformed to the stable form of titanocene, $(CpTiH)_2(C_{10}H_8)$, in 40% yield. Reaction with HCl gives a mixture of Cp_2TiCl and Cp_2TiCl_2, while H_2 gives a gray-green hydride, apparently similar to the previously-reported $(Cp_2TiH)_x$. In the absence of a good coordinating solvent, the dimer absorbs molecular nitrogen with the stoichiometry 2 (Ti_2): 1 N_2; this does not form in THF, suggesting the N_2 coordinates to the same site as THF (the Ti(II) centers). Reduction of the coordinated N_2 was discussed earlier. $Cp_3(C_5H_4)Ti_2$ is a very effective catalyst for hydrogenation and isomerization of olefins, with activity comparable to polymer-supported titanocene catalysts (vide infra) (12).

Interpretation of the bonding in bent bis(cyclopentadienyl) complexes, Cp_2MX_n, continues to attract interest. A mostly qualitative MO study of such species includes examples from group IVa (42). Crystal structures have been determined for $Cp_2Ti(S_5)$ and $Cp_2Ti(SPh)_2$, as well as the vanadium analogs (43,44). In both cases the S-M-S angle is about 5° larger for the Ti complex, in agreement with the conclusion based on EPR studies, reported last year, that the unpaired electron in the vanadium(IV) complexes resides primarily in an orbital lying outside the region between the X ligands, contradicting the older Ballhausen-Dahl model.

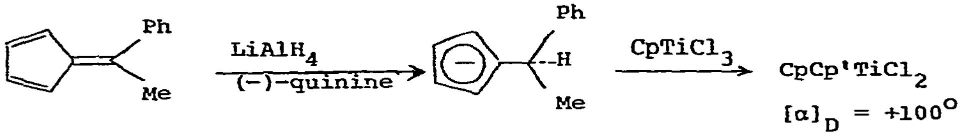
A further interesting feature in the $Cp_2Ti(S_5)$ structure is the 6-membered TiS_5 ring, which has a chair conformation. As a result, the two Cp rings are non-equivalent (axial and equatorial positions) and, in fact, the NMR shows two distinct peaks at room temperature; also the Ti-Cp ring distances are significantly different (44). An independent synthesis of this compound was achieved by photolyzing Cp_2TiR_2 (R = CH_3, CH_2Ph) with S_8; the Zr analog gave an uncharacterized product which contains S but is not the same complex (45). A number of sulfide complexes $Cp_2Ti(SR)_2$ were prepared from $Cp_2Ti(CO)_2$ and RSSR; at higher temperatures this reaction leads to $(Cp_2Ti(SR))_2$ (46).

Both intra- and intermolecular Cp exchanges have been examined. A complex with bridged Cp ligands, $(\eta^5-C_5H_4-CH_2CH_2CH_2-\eta^5-C_5H_4)TiCl_2$, reacts with NaCp to give



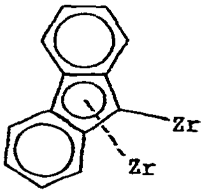
which on cleavage with HCl or CCl_4 gives only the original bridged dichloride and no Cp_2TiCl_2, indicating that there is no exchange of η^5- and η^1-bonding roles between the bridged and orginary Cp groups. In contrast, the product obtained from Cp_2TiCl_2 and $[(CH_2)_3(C_5H_4)_2]^{2-}$ shows a more complicated NMR and gives, upon treatment with CCl_4, 70% bridged and 30% ordinary Cp_2TiCl_2. This ratio does not change with time, so the $\eta^5-\eta^1$ exchange must occur during formation (47). Cp rings are exchanged between $(\eta^5-C_5H_5)_2TiCl_2$ and $(\eta^5-C_5D_5)_2TiCl_2$ under photolysis, with a quantum yield of only ca. 10^{-2}. The reaction of Cp_2TiCl_2 with methanol to give $CpTiCl_2(OMe)$, previously reported to go thermally, was shown to occur only with irradiation (48).

The group at Dijon continues to report studies on chiral cyclopentadienyl systems. One class of compound studied contains a chiral ring, 1-methyl-(2 or 3)-isopropylcyclopentadienyl, so that complexes CpCp'TiXY (X, Y = aryloxo or Cl^-) can be separated into diastereomers. The reaction CpCp'Ti(OAr)(OAr') + HCl $\longrightarrow$ CpCp'Ti(OAr)Cl + HOAr' was found to go with retention at Ti. Crystal structures of two examples of this class were reported (49). A different type of system, containing a chiral side-chain on a ring, was prepared as follows:



The optical purity of the anion was estimated to be 17% by comparing the substituted ferrocene derived therefrom. Conversion of the dichloride to CpCp'TiClX (X = C_6F_5 or o-$CH_3C_6H_4O$−) gives diastereomers, for which a crystal structure determination led to assignment of absolute configuration at Ti (50). Reduction of either diastereomer of CpCp'TiCl(C_6F_5) to the Ti(III) complex, followed by reoxidation with CCl_4, results in complete loss of stereospecificity (51). A theoretical (CNDO) study on a variety of MX_4, MX_3^-, $MX_3\cdot$ and MX_3^+ systems (M = C, Si, Ti) may be of relevance to these systems: calculations suggest TiX_3^+ cations, including $CpTiCl_2^+$, should be pyramidal rather than planar; hence it is conceivable that the exchange reaction with retention cited above could proceed through a cationic, "three-coordinate" intermediate (52).

A fluorenyl complex, $(C_{13}H_9)_2Zr(CH_3)_2$, was prepared by reacting fluorenyl-lithium with $ZrCl_4$ and treating the resulting dichloride in situ with $LiCH_3$. The NMR shows the methyl signals at 12.06τ, attributed to shielding by ring-current effects of the non-coordinated six-membered rings. Photolysis leads to methane evolution and formation of a diamagnetic product analyzing as bis(fluorenyl)zirconium. Both NMR and IR indicate that no proton is present on the 9-carbon; an (η^5,η^1)-bridging structure, reminiscent of that found in niobocene, was suggested:



The hafnium analog was also generated but appears to be much less stable (53).

Several useful preparative papers have appeared during the last year. Convenient routes to the highly substituted cyclopentadienyls, C_5Me_5 and C_5Me_4Et, have been worked out; the latter was used to prepare $(C_5Me_4Et)_2TiCl_2$, which is much more soluble in non-polar solvents than the C_5Me_5 analog (54). Reaction of $TiCl_3$ with TlCp in refluxing THF provides the best method yet found for preparing Cp_2TiCl, as well as the analogous V(III) and Sc(III) compounds (55). Preparative details for $(CpTiCl_2)_n$ and $CpTiCl_2(PMe_2Ph)_2$ have been reported (56).

In an attempt to generate $[Cp_2Ti]^{2+}$ by treating Cp_2TiCl_2 with $AgBF_4$ or $AgPF_6$, red compounds were obtained which yielded, on workup with methanol, only Cp_2TiF_2. The latter could be reconverted to the red species with BF_3 or PF_5 in CH_2Cl_2. These red compounds are formulated as Cp_2TiX_2, where X = BF_4 or PF_6; they show neither conductivity in solution nor coupling in the NMR between the fluorines and the Cp protons, suggesting the bonding cannot be described either as purely ionic or purely covalent (57). A cationic Ti(III) species was generated by the following reaction:

$$Cp_2TiCl + Zn(B_{10}H_{12}) \xrightarrow[Me_2CO]{THF} [Cp_2Ti(THF)(Me_2CO)]_2{}^{+}[Zn(B_{10}H_{12})_2]^{2-}$$

The crystal structure shows tetrahedral coordination about Ti (58), as in the related $[Cp_2Ti(CH_3OCH_2CH_2OCH_3)]^+$ reported last year.

The borohydride $Cp_2Zr(BH_4)_2$ can be prepared from the dichloride either with $LiBH_4$ in benzene (preferable) or with $NaBH_4$ in THF; vibrational spectra and differential thermal analysis are reported (59). Reaction of Cp_2TiCl with $LiAlH_4$ gives Cp_2TiAlH_4 (60), while several cyclopentadienyltitanium(IV) halides have been reduced to Ti(III) with aluminum hydrides (61).

A number of complexes with oxygen- or sulfur-donor ligands have been reported. Reaction of Cp_2TiCl_2 with one equivalent of ethanol at room temperature gives $CpTiCl_2(OEt)$ in 83% yield; the facile removal of an η^5-Cp group instead of Cl replacement is notable. Excess EtOH leads to $CpTiCl(OEt)_2$ at room temperature and $Ti(OEt)_4$ at reflux. Similar derivatives of glycols and β-diketonates were prepared (62). Polymers can be generated by reacting Cp_2ZrCl_2 with aromatic diols (63). Reaction of Cp_2TiCl_2 with $Co_2(CO)_8$ in benzene at 50° gives the interesting bimetallic compound $Cp_2TiCl(OC(Co_3(CO)_9))$ where the carbonylcobalt cluster is behaving as an alkoxo ligand; the crystal structure shows unexceptional coordination about Ti (64). A stopped-flow kinetic study was performed on the hydrolysis of $Cp(\eta^5\text{-}C_5H_4CH_3)TiCl_2$ to $[CpCp'Ti(OH)]^+$ (65). Aroyl peroxides react with "Cp_2Ti" or Cp_2TiPh_2 to give $Cp_2Ti(O_2CAr)$; a crystal structure was determined for Ar = *p*-nitrophenyl (66). Preparation of Cp_2ZrClX, X = acetate, trifluoroacetate or bromide, was reported (67). Cp_2TiCl_2 reacts with potassium xanthates to give air-sensitive $Cp_2Ti(S_2COR)_2$ (68). A crystal structure shows that $CpZr(S_2CNMe_2)_3$ has a distorted pentagonal bipyramidal geometry with the Cp in an axial position; the NMR shows four methyl resonances, indicating some stereochemical rigidity, unusual for this type of structure (69).

Bromination of cyclopentadienyltitanium alkoxides can follow several paths: $(\eta^5\text{-}C_5Me_5)Ti(OEt)_3$ plus two moles of Br_2 gives, upon irradiation, $Cp'TiBr_3$, while the ordinary Cp analog gives $TiBr_2(OEt)_2{\cdot}EtOH$, and $CpTi(OPh)_3$ gives $CpTiBr_2(OC_6H_4Br)$; with excess Br_2 the last compound gives $CpTiBr_3$ and dibrominated phenols (70). Titanium-germanium bonds can be cleaved by chlorocarbons, either thermally or photochemically; *e.g.*, photolysis of $Cp_2Ti(GePh_3)_2$ with CH_3Cl gives initially Ph_3GeCl

and $Cp_2TiCl(GePh_3)$ and, more slowly, Cp_2TiCl_2 (71). $CpTiBr_3$ forms a mono-THF adduct; in the NMR the THF protons are split in a 1:1:2 pattern, attributed to hindered rotation. The analogous iodide gives a di-THF adduct, while the fluoride and chloride do not interact with THF (72).

A ^{13}C NMR study was carried out for $CpTiX_3$, Cp_2TiX_2 and $(\eta^5\text{-}C_5Me_5)TiX_3$ compounds (X = halide or alkoxide); trends in shifts as a function of ligand were compared to ^1H NMR results (73). ^{13}C NMR studies on $Ti(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)$ suggest that the C_7 ring is more shielded, in contrast to the Cr analog; this result was correlated with preferential sites for metallation (74). The heat of formation of Cp_2TiCl_2 was determined and used to estimate the mean Ti-Cp dissociation energy (75). A negative ion mass spectral study was reported for a group of cyclopentadienyltitanium(IV) complexes (76).

OTHER π-BONDED COMPLEXES

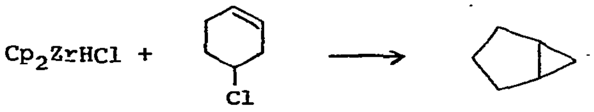
Co-deposition of titanium vapor and cycloheptatriene gave $Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$ in 46% yield; this compound had been previously obtained by solution methods. Reaction of Ti vapor with a mixture of benzene and cycloheptatriene gave only the above and $Ti(\eta^6\text{-}C_6H_6)_2$; no mixed-ring compounds were obtained (77).

A full paper reports on the metallocarboranes $[M(C_2B_{10}H_{10}R_2)_2]^{2-}$ (M = Ti, Zr, Hf; R = H, CH_3); $[CpTi(C_2B_{10}H_{12})]^-$; $[(\eta^8\text{-}C_8H_8)Ti(C_2B_{10}H_{12})]^{n-}$ and $[(\eta^8\text{-}C_8H_8)Ti(C_2B_9H_{11})]^{n-}$ (n = 0,1), whose preparation and properties were described in several communications surveyed last year. Studies on visible, IR and NMR spectroscopy, magnetic properties and electrochemical behavior were discussed in detail (78). Tris(pyrazolyl)borate, $[HBPz_3]^-$, reacts with $TiCl_4$ to give $(HBPz_3)TiCl_3$, an analog of $CpTiCl_3$; further reaction to $(HBPz_3)_2TiCl_2$ was not observed, presumably because of the greater ligand bulk compared to Cp. Ti(III) complexes $(HBPz_3)TiCl_2(THF)$ and $[(HBPz_3)TiCl(OCH_3)]_2$ were also prepared (79).

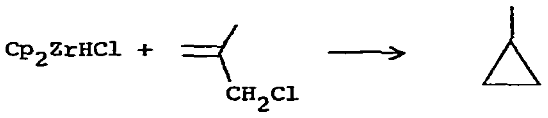
A communication reports on the intercalation of several sandwich compounds, including $CpTi(C_8H_8)$, into ZrS_2. Only compounds with relatively low ionization potentials appear to be able to form such intercalation compounds, but this is not the only factor involved (80).

APPLICATIONS IN SYNTHESIS AND CATALYSIS

The addition of Cp_2ZrHCl to unsaturated molecules ("hydrozirconation") continues to attract attention. A review on this reaction and its synthetic applications has appeared (81). The compatibility of the reagent with functional groups has been investigated: $R_2C{=}O$, $RC{\equiv}N$ and RCO_2H react to give complexes Cp_2ZrClX where $X = R_2CHO-$, $RCH{=}N-$ and RCO_2-, respectively. Esters RCO_2R' give a mixture of $Cp_2ZrCl(OCH_2R)$ and $Cp_2ZrCl(OR')$; CO_2 is reduced to formaldehyde, with formation of $(Cp_2ZrCl)_2O$; cyclopentadiene gives Cp_3ZrCl; ethylene oxide gives $Cp_2ZrCl(OCH_2CH_3)$. Reaction with the unsaturated ketone, $FcCOCH{=}CHCH_3$ (Fc = ferrocenyl) followed by hydrolysis gives mostly (96%) the rearranged product $FcCH{=}CHCH(OH)CH_3$, along with a small amount of $FcCOCH_2CH_2CH_3$; it is not known how the rearrangement occurs (82). In some cases, treatment of halogen-containing alkenes with Cp_2ZrHCl leads to cyclopropanes by γ-ZrX elimination; *e.g.*,



(40%)

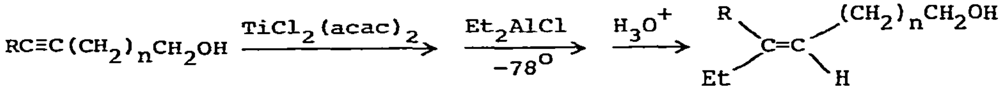


(31%)

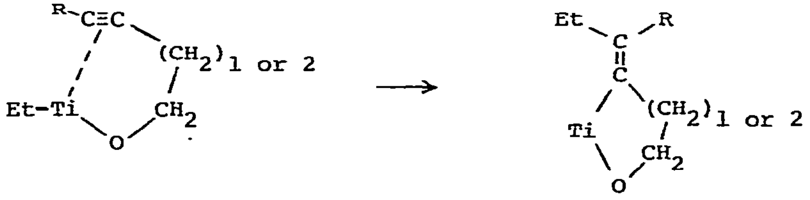
Alkenes and alkanes are also produced. 1-chlorocyclohexene gives only reduction (83).

A zirconium-catalyzed hydroalumination can be achieved by reacting terminal olefins with $LiAlH_4$ in the presence of small amounts of $ZrCl_4$; subsequent treatment with aqueous acid or halogen leads to the alkane or alkyl halide. The reaction is proposed to involve generation of a Zr-H species, addition to the olefin to give Zr-R, and transfer to Al to give Al-R. No organozirconium products could be detected even with equimolar $ZrCl_4$; under the latter conditions isomerization of 1-hexene to 2-hexenes was observed (84). This behavior is opposite to that found for Cp_2ZrHCl, which migrates to the least substituted carbon on adding to an olefin (81); presumably the difference results from greater steric bulk of the latter Zr group. A mixture of $LiAlH_4$ with either $TiCl_4$ or Cp_2TiCl_2 effects the reduction of terminal olefins and of alkynes, but not internal olefins (85).

A Ti-catalyzed alkylation of alkynols results from the following sequence:

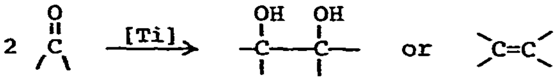


The reaction does not go without Ti and only works if n = 1 or 2; an intermediate such as

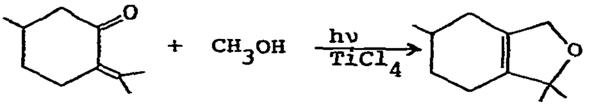


was suggested (86).

Several studies report on the condensation of carbonyl compounds to pinacols (87) or olefins (88-90) using various forms of low-valent Ti:



$TiCl_4$ has been found to induce novel photocoupling reactions, e.g. (91)



(62%)

It is not known whether organotitanium intermediates are involved in any of the above reactions.

A full paper discusses the preparation and catalytic use of polymer-bound cyclopentadienyl complexes Ⓟ-Cp-MCl_3 (M = Ti, Zr, Hf) and Ⓟ-Cp-$TiCpCl_2$, where Ⓟ-Cp represents a cyclopentadienyl group covalently linked to a polystyrene bead. Electron-microprobe X-ray fluorescence analysis was used to show that the metal complex becomes uniformly distributed throughout a bead. Olefin hydrogenation catalysts were prepared by reducing Ⓟ-Cp-MCl_3 with LiBu; the Ti system showed up to 100-fold greater activity than the catalyst derived from reduction of monomeric $CpTiCl_3$ if powdered beads were used. The Zr and Hf species were much less active (92).

Ziegler polymerization catalysts prepared from cyclopentadienyl metal complexes and trialkylaluminum were found to be considerably improved in activity by addition of small amounts of water. With a Zr-containing system, the molecular weight of the polymers obtained could be controlled over a wide range by varying the temperature (93). Polarographic techniques for determining the oxidation state of Ti in the butadiene polymerization catalyst $Ti(OR)_4$-$Al(Bu^i)_3$ were described (94).

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