TITANIUM, ZIRCONIUM AND HAFNIUM

ANNUAL SURVEY COVERING THE YEAR 1977 *

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This survey follows the 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. The abbreviations Cp (for η^5-cyclopentadienyl) and Cp' (for any ring-substituted cyclopentadienyl group) have been used throughout.

A review entitled "Recent Advances in the Organometallic Chemistry of Titanium" has appeared in the J. Organometal. Chem. Library series (1). A recent volume of the Gmelin series covers alkyl, allyl and mono-Cp titanium compounds (2).

CARBONYL AND DINITROGEN COMPLEXES

The binary compounds $Ti(CO)_6$ and $Ti(N_2)_6$ have been generated by matrix isolation techniques and studied spectroscopically. Both show two infrared bands assigned to ligand stretching (ν_{CO} 1985, 1947; ν_{NN} 2131, 2100 cm^{-1}); the splitting was attributed to Jahn-Teller distortion expected for a low-spin d^4 system. The ligand field splitting is substantially larger for CO than N_2 (28255 vs. 21370 cm^{-1}). $Ti(CO)_6$ decomposes to Ti atoms and CO at about 40°K (3).

Full details of the crystal structure of $Cp_2Ti(CO)_2$ have been reported (4). Oxidative addition reactions of this compound

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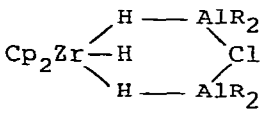
have been examined: both RCOCl (R = Me, Ph) and RX (R = Me, Et, *i*-Pr, *s*-Bu) react to give acyls, $Cp_2Ti(COR)X$. The crystal structure of $Cp_2Ti(COMe)Cl$ was determined and is very similar to the Zr analog, with a side-bonded, formally three-electron acyl ligand. A nucleophilic displacement mechanism was proposed for the alkyl halide reactions, although a process involving radicals appears equally plausible. In fact, benzyl chloride and Ph_2PCl give as products Cp_2TiCl_2 and bibenzyl or Ph_2PPPh_2 respectively, a result which seems more in accord with a radical pathway. Other reactions reported are with $MeSO_2Cl$, HOAc and phenanthrene-9,10-quinone (5). In contrast, $Cp_2Zr(CO)_2$ reacts with MeI without CO insertion, to give Cp_2ZrMeI. Reaction with PMe_3 affords $Cp_2Zr(CO)(PMe_3)$; diphenyl acetylene gives the metallocycle $Cp_2Zr(C_4Ph_4)$; the presumed intermediate $Cp_2Zr(CO)$-(PhCCPh) (previously isolated for Ti) could not be detected. The far-infrared spectra of these molecules were examined (6).

Two further examples of CO hydrogenation in Group IV metal systems, first reported last year, have been discovered. Heating $Cp_2Ti(CO)_2$ under hydrogen produces methane, while the metal complex is converted to an inactive species characterized by X-ray crystallography as $(CpTi)_6O_8$: an octahedron of Ti atoms, each with a η^5-Cp bonded, and a μ_3-O on each face (7). Reaction of Cp_2ZrCl_2 with *i*-Bu_2AlH affords a mixed-metal species, assigned the following structure based on NMR;



related species formed from Cp_2ZrH_2 or Cp_2ZrR_2 were also studied (8). The above compound absorbs 2 moles of CO per Zr to give a solution which on hydrolysis affords a mixture of linear alcohols, $CH_3(CH_2)_nOH$ (n = 0-3). Addition of excess *i*-Bu_2AlH causes more CO to be taken up (9). With last year's report, there are now models based on Group IV metals for the various catalytic CO reductions - methanation, methanol synthesis, and homologation (Fischer-Tropsch process), although none of these involve catalytic use of hydrogen.

Studies on the use of reduced titanium systems in N_2 activation continue. Reaction of Cp_2TiCl with RMgCl gives solutions which react further with reducing agents (sodium naphthalenide or *i*-PrMgX) under N_2 to give reduced forms of nitrogen, N_2H_4 and NH_3. A nitrogen adduct, stable below -60°, was isolated only for R = CH_2CMe_3. Formation of NaCp or CpMgCl was also observed, suggesting that generation of the active species involves reductive removal of one or more Cp groups (10). The species obtained from the reduction of Cp_2TiCl_2 with Mg under N_2 reacts with CO_2 to give a compound formulated as $Cp_2Ti(NCO)$ plus $Cp_2Ti(CO)_2$; the latter was the sole product when the initial reduction was carried out under Ar (11).

ALKYL AND ARYL COMPLEXES

Compounds Cp_2TiR, Cp_2MR_2 and Cp_2MRCl (M = Zr, Hf; R = $CHPh_2$, $CH(SiMe_3)_2$ were prepared and studied by ESR (Ti) or NMR. Crystal structures for R = $CHPh_2$, M = Zr and Hf were reported. For Zr the metal-carbon distance (2.388 $\mathring{A}$) is substantially longer than in the methyl analog, whereas in Hf no lengthening is observed (12).

A series of alkenyl complexes MR_4 (Ti, Zr, Hf), Cp_2MR_2 (Ti, Zr) and Cp_2ZrRCl were prepared for R = $-C(Ph)=C(Me)_2$. Insertion reactions with MeNC are also reported (13). Reaction of $TiCl_4$ with $LiCH_2CN$ gives $[Ti(CH_2CN)_4 \cdot 2\ THF]_n$, apparently polymeric; in pyridine solution the NMR shows three singlets indicating a complex structure (14). Photoelectron spectra of a number of methyltitanium compounds ($MeTiCl_3$, $MeTi(OR)_3$, $MeTiCp(OR)_2$, $MeTi(NR_2)_3$) have been measured and correlated with CNDO calculations (15). $MeTiCp(OR)_2$ was prepared by several routes and its reactivity towards I_2, ROH, O_2 and SO_2 examined (16).

Reaction of $CpTiCl_3$ with 3-butenylmagnesium bromide gives $CpTi(CH_2CH_2CHCH_2)_3$ which is a catalyst for ethylene oligomerization (17). Treatment of Cp_2TiCl_2 with C_8H_8 and i-PrMgCl produces $Cp_2Ti(C_8H_9)$, suggested to contain a η^1-cyclooctatrienyl ligand because of differences in the IR spectrum compared to $Cp_2Nb(\eta^3\text{-}C_8H_9)$. A mechanism involving insertion of C_8H_8 into a Ti-H bond, formed by β-H elimination from an (i-Pr)Ti intermediate, was proposed (18). Ferrocenyllithium reacts with Cp_2MCl_2 to give $Cp_2M(Fc)_2$ (M = Ti, Zr, Hf); the color of these compounds (green for Ti, red for Zr and Hf) was interpreted as resulting from a charge transfer transition from a ferrocene to a Cp_2M orbital (19).

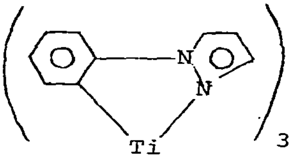
A number of studies have focussed on alkyl complexes of metals in oxidation states less than +4. Treatment of $TiCl_3$ with $LiCH_2SiMe_3$ gives only $Ti(CH_2SiMe_3)_4$, plus a precipitate apparently consisting mostly of TiR_2 species (20). R_3Ti was generated by the following scheme:

$$TiR_4 + R'Li \xrightarrow[2\ hrs]{25°} TiR_3 + RLi + 1/2\ R'H + 1/2(R'\text{-}H)$$

where R is an alkyl group with no β-hydrogen (CH_2SiMe_3, CH_2Ph) and R' <u>does</u> have a β-hydrogen (CH_2CH_3). TiR_3 could be isolated by quenching RLi with CO_2; otherwise TiR_4^- forms. Characterization is based on reaction with I_2 which gives 3 RI/Ti, and an IR spectrum which was interpreted in terms of D_{3h} symmetry. This interpretation appears questionable, especially in light of the fact that the species show no ESR and have ^1H NMR quite similar to TiR_4 (21). Assuming the empirical formula is correct, these results suggest a dimeric (at least) structure to explain the apparent diamagnetism. Reaction of $TiCl_n$ (n = 2-4) with

$LiCPh_3$ or with "hexaphenylethane" gives trityl complexes, $(Ph_3C)TiCl_{2,3}$ (22).

Reaction of $TiCl_3$ with excess mesityllithium gives an "ate" complex, $LiTi(mes)_4 \cdot 4$ THF, which reacts with O_2 to give neutral $Ti(mes)_4$ (23). Metallation of N-phenylpyrazole with EtMgBr, followed by treatment with $TiCl_3$, gives the chelated Ti(III) alkyl (24):



Other Ti(III) chelates include (dipivaloylmethanato)Ti($\underline{o}$-$C_6H_4CH_2$-$NMe_2)_2$ (25) and $Cp_{3-n}Ti(CH_2C_6H_4$-$\underline{o}$-$NMe_2)_n$ (n = 1, 2); the latter (n = 1) shows a doublet in the ESR, indicating only one of the two methylene protons is coupled; the reason for this nonequivalence is unclear (26). The Zr(II) complex $Ph_2Zr \cdot OEt_2$ is stable to halocarbons, in contrast to the Ti and V analogs (27).

The metallocycle $Cp_2Ti(CH_2)_4$, which was the subject of a full paper last year, has been reexamined and found to undergo exchange with substituted olefins, giving substituted titanacyclopentanes. This suggests that the metallocycle is in equilibrium with a bis(olefin)Ti(II) complex in which olefin exchange can occur (28). The reaction of Ti and Zr chlorides with the phosphorus ylide Me_3PCH_2 has been studied; in addition to $Cp_2\overline{Ti(CH_2PMe_2CH_2})$ which was reported last year, complexes with the following formulae were obtained: $Cl_2\overline{Ti(CH_2PMe_2CH_2})_2$; $[(Me_2N)_2Ti(CH_2PMe_3)_2]^{2+}Cl_2^-$; $(Me_2N)_2Ti(\mu\text{-}CPMe_3)_2Ti(NMe_2)_2$; $[(Me_2N)_2Ti(\mu\text{-}CPMe_3)(\mu\text{-}CHPMe_3)Ti(NMe_2)_2]^+Cl^-$; and $[Cp_2M(CH_2PMe_3)_2]^{2+}$-$Cl_2^-$ (M = Ti, Zr) (29).

Photolysis of Cp_2TiMe_2 in the presence of PhCCPh gives an insertion product, $Cp_2Ti(CPh{=}CMePh)Me$, in addition to the previously found metallocycle $Cp_2Ti(C_4Ph_4)$. With $(C_6F_5)CC(C_6F_5)$ the insertion product was the only organometallic product observed

(30). A full paper has appeared on carbonylation reactions of Cp_2MR_2 (M = Zr, Hf; R = Me, CH_2Ph, Ph); formation of $Cp_2M(COR)R$ is reversible for the alkyl compounds but irreversible for R = Ph. Equilibrium and thermodynamic data were obtained for the former. The failure to eliminate ketone RCOR, as occurs in the Ti analog, was interpreted in terms of stabilization resulting from the side-bonded acyl group, demonstrated for $Cp_2Zr(COMe)Me$ by a crystal structure (31). Carbonylation of tetraallylzirconium gives two products, analyzing approximately as $(C_3H_5CO)_3Zr$ and $(C_3H_5)_2(C_3H_5CO)_2Zr$; spectroscopic studies led to no conclusive structural assignments (32).

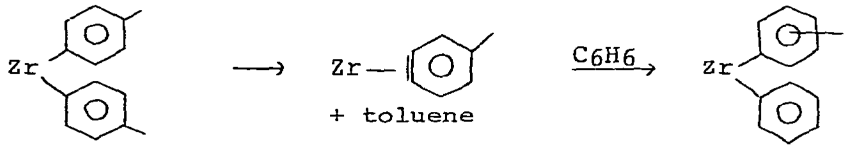
$RTiBr_3$ (R = Me, Ph, p-tolyl) forms 1:1 and/or 1:2 adducts with nitriles, phosphines, ethers and thioethers (33). Cp_2TiR forms blue or green 1:1 adducts with nitriles R'CN; in some cases these go on to form yellow species which appear to be dimeric Ti(IV) complexes, but their exact nature is uncertain (34). Reaction of $Cp_2Zr(CH_2Ph)_2$ with $HgCl_2$ gives a species analyzing as $Cp_2ZrCl_2 \cdot 3PhCH_2HgCl$ (35).

Decomposition pathways for Cp_2MR_2 systems continue to attract interest. Photolysis of Cp_2TiMe_2 affords methane; the additional hydrogen atoms were shown by deuterium labeling to come from Me or Cp groups but not from solvent. In addition, a black compound analyzing as $C_{10}H_{9-10}Ti$ was obtained; chemical and spectroscopic studies suggest that this "titanocene" is related to $(C_5H_5)_3(\mu-C_5H_4)Ti_2$, whose structure was reported last year, but probably not identical; a molecular weight determination in benzene suggests the formulation $(C_{10}H_xTi)_4$ (36). On the other hand, an ESR study of photogenerated intermediates from Cp_2MR_2 (M = Ti, Zr, Hf; R = Me, CH_2Ph) seems to indicate homolysis of the M-R bond occurs. For M = Ti, a singlet (with hyperfine satellites due to ^{47}Ti and ^{49}Ti) characteristic of Ti(III) was observed, and adducts of R· with spin traps could be obtained. For Zr and Hf similar results were observed, except that the ESR signal is a doublet (splitting 7G), attributed to formation of Cp_2MH (37). These two studies appear inconsistent: if R· formation is indeed a significant pathway (quantitative measurements suggest the paramagnetic products constitute as much as 10% of the total (37)) then <u>some</u> RH formation <u>via</u> H-abstraction from solvent would be anticipated. Further examination appears warranted.

Thermal decomposition of Cp_2ZrR_2 gives analogous results: RH is formed with H coming from Cp and R but not solvent (toluene); a black, diamagnetic metal-containing product is obtained; ESR-active intermediates were observed (38). An interesting exchange reaction was observed from Cp_2ZrAr_2 (Ar = aryl) in arene solvents:

$$Cp_2ZrAr_2 \xrightarrow[70°]{Ar'H} Cp_2Zr(Ar,\ Ar')_2 \xrightarrow{h\nu} \text{biaryls}$$

Exchange was studied by photolyzing the complex and analyzing the biaryls formed. For Ar = p-tolyl and Ar'H = benzene, both (p-tol-Ph) and (m-tol-Ph) were obtained, suggesting an aryne intermediate as in the following scheme (Cp's omitted) (39):



<u>CYCLOPENTADIENYL COMPLEXES</u>

Reaction of the stable form of titanocene with HCl gives $(CpTiCl)_2(C_{10}H_8)$, characterized by X-ray crystallography, analogous to the hydroxo-bridged dimer reported last year. Contrary to some previous reports, the compound was found to be strictly diamagnetic, in spite of the very long Ti-Ti distance (3.638 Å); superexchange <u>via</u> a bridging ligand was proposed (40). This may be compared with the related Ti(III) dimers $[Cp_2TiCl]_2$, $[(MeCp)_2TiCl]_2$, and $[(MeCp)_2TiBr]_2$: all have <u>longer</u> Ti-Ti distances, and all are antiferromagnetic, with only partial correlation between exchange energy and metal-metal distance (-J = 111, 160, 138 cm^{-1}; Ti-Ti = 3.956, 3.926, 4.125 Å respectively), suggesting both direct and superexchange mechanisms (41). In light of these results, direct exchange in the fulvenide-bridged dimer may not be unreasonable.

An electron diffraction study on Cp_2MCl_2 (M = Ti, Zr) is in reasonable agreement with X-ray results (42). A redetermination of the crystal structure of $(CpTiCl_2)_2O$ confirms the linearity of the Ti-O-Ti group (43). The crystal structure of $Cp_2Ti(N_3)_2$ shows no unusual features (44).

Cp ring exchange has been the subject of several studies. Treatment of Cp_2MCl_2 (M = Ti, Zr, Hf) with 2 equivalents of NaC_5D_5, followed by HCl, gives a mixture of $(C_5H_5)_2$-, (C_5H_5)-(C_5D_5)- and $(C_5D_5)_2MCl_2$, indicating (as expected) that exchange within Cp_4M is fast. Similar exchange was observed with $NaC_5H_4CH_2Ph$; this technique can be used to prepare polymer-supported metallocenes (45). A detailed study shows that these reactions are much more complex than first appears. For example, reaction of Cp_2TiCl_2 with 2NaCp' (Cp' = C_5H_4Me), followed by cleavage with CCl_4, gives the following metallocene dichlorides: 45% Cp_2, 30% CpCp', 25% Cp'_2. The reverse reaction, Cp'_2TiCl_2 + 2NaCp, gives a different mixture: 15% Cp_2, 40% CpCp', 45% Cp'_2; these results are clearly incompatible with a sole mechanism involving Cp_4M as intermediate, in which rapid η^1-η^5 ring exchange occurs. It was suggested that this exchange might be slow if some of the rings are substituted, in contrast to Cp_4M which shows rapid exchange on the NMR time scale slightly above room temperature. Exchange was also observed on reacting $Cp_2Ti(OR)_2$ with NaCp', leading to (CpCp')- and $Cp'_2Ti(OR)_2$ and showing that exchange can occur by direct ring displacement without going through Cp_4M-type species. Even a mixture of Cp_4Ti and Cp'_4Ti gives exchange: CCl_4 treatment gives $CpCp'TiCl_2$ as well as the symmetric dichlorides (46). Although no unified scheme could be proposed to account for all the various results, it seems clear that a number of pathways are involved in these reactions.

Cp ring exchange can also be effected photochemically: irradiation of mixtures of Cp_2MCl_2 and Cp_2MCl_2-d_{10} (M = Zr (47) and Hf (48)) causes formation of Cp_2MCl_2-d_5. The quantum yield for these reactions is only ca. .02.

Work on Cp systems containing elements of chirality continues unabated. Complexes in which the chiral element is a ring substituent, Cp' = $C_5H_4CHMePh$ (49); the ring itself, Cp' = 1,2- or 1,3-C_5H_3Me(*i*-Pr) (50,51); or the metal as in CpCp'TiCl(C_6F_5) (52) and CpCp'HfCl(CH_2Ph) (53) have been prepared, separated into isomers, and in some cases characterized by crystallographic studies (50,54). Stereochemistry of some reactions has been examined; for example, the reaction of CpCp'TiCl(OAr) with NaOAr' gives symmetrization, epimerization and (OAr)-exchange as well as the desired Cl-replacement, while treatment of CpCp'Ti(OAr)(OAr') with HCl gives varying degrees of selective (OAr)-cleavage and stereospecificity (retention) depending on the nature of the aryl groups (54).

Another convenient route to highly substituted cyclopentadienes, C_5Me_4RH (R = Me, Et, Pr, Bu, Ph) has been reported, involving simply treating RCO_2R' with two equivalents of 2-lithio-2-butene followed by hydrolysis; various Cp'_2MCl_2 (M = Ti, Zr) were prepared (55). An attempt to make complexes of $C_5H_4CMePh_2$ led instead to Cp'_2MCl_2 where Cp' = $C_5H_4C(Ph)=CH_2$; the unsaturated side group can be hydrogenated over PtO_2 (56). Complexes Cp'_2MCl_2 with Cp' = $C_5H_{5-n}(SiMe_3)_n$ were prepared for n = 1 and 2 (57). From the cyclopentadienyl ylide $C_5H_4PPh_3$, complexes of formula Cp'_2TiCl_4 (probably $[(C_5H_4\overset{+}{P}Ph_3)_2TiCl_2]Cl_2$, $Cp'TiCl_3$ and $Cp'MCl_4$ (M = Zr, Hf) were prepared (58).

An electron diffraction study on $Cp_2Ti(BH_4)_2$ shows longer

Ti-C and shorter Ti-B distances than the earlier X-ray determination; results are in somewhat better agreement with a structure in which the BH_4 groups are bidentate (59). An X-ray study on $CpTiCl(BH_4)$ shows it to be a dimer with bridging Cl's and tridentate BH_4 groups (60).

The coordination preference of the CpTi(III) moiety was investigated by treating $CpTiCl_2$ with $NaBPh_4$ in CH_3CN or pyridine; in both cases the product obtained was $[CpTi(solvent)_5]^{2+}(BPh_4)_2$ (61). $Cp_2Ti(OAr)$ was prepared from Cp_2TiCl and NaOAr or by reducing $Cp_2TiCl(OAr)$ with Zn; reducing the latter with Al gives Cp_2TiCl instead. $Cp_2Ti(OAr)$ reacts with RSSR to give $Cp_2Ti(OAr)(SR)$ as well as symmetrization products (62). The aqueous chemistry of Cp_2TiX_2 has been studied for halide exchange reactions (63).

The crystal structure of $CpTi(O_2CPh)_4TiCp$ is similar to the vanadium analogs, with four bridging carboxylate groups; the Ti-Ti distance (2 crystallographically independent molecules, 3.63 and 3.74 Å) was interpreted as showing no metal-metal bond (64). Several Zr carboxylates, $Cp_2ZrCl(O_2CR)$ (R = CH_3, CF_3) and $CpZr(OAc)_3$, have been prepared (65). Complexes CpTiClL have been reported where L is a potentially chelating Schiff base (66). An independent preparation of $CpZr(S_2CNR_2)_3$, whose synthesis and crystal structure were reported last year, has appeared (67).

The electronic spectra of Cp'_2TiX_2 (X = Cl, OAr) have been compared to CNDO/2 calculations; all absorptions can be assigned to ligand-to-metal charge transfer (68). Chronopotentiometric studies on Cp_2TiCl_2 show a reversible one-electron reduction (69). The radiochemistry (Szilard-Chalmers reaction) of Cp_2MCl_2 and analogs with linked Cp rings has been examined (70).

OTHER π-BONDED COMPLEXES

The reaction of $TiCl_4$ with olefins has been investigated by ion cyclotron resonance. Among the processes detected are formation of diene complexes by H_2 elimination, formation of allyl complexes by HCl elimination, and fragmentation of longer olefins (71).

An INDO SCF calculation on $CpTi(\eta^8-C_8H_8)$ suggests formulation as Ti(III), with the HOMO mostly Ti d_{z^2} in character, in agreement with ESR results. Also the Cp ring is less negatively charged than the 8-membered ring, in agreement with the observed preferential metallation at the former (72).

APPLICATIONS IN SYNTHESIS AND CATALYSIS

Last year saw a new development in the hydrozirconation reaction: the use of mixed-metal systems, in which a zirconium alkyl is formed and the alkyl group transferred to another metal. This offers the advantages of the ready formation of the Zr-alkyl as well as the frequently greater versatility of other alkyl metal reagents. Thus $Cp_2ZrCl(R)$ (R = alkyl or alkenyl) reacts with $AlCl_3$ to give an alkyl aluminum species which is acylated with R'COCl to give ketones, R'COR, in up to 98% yield. In contrast, direct acylation of the Zr compounds works poorly (R = alkyl) or not at all (R = alkenyl). The transmetallation step goes with retention of configuration at carbon and is faster for alkenyls, suggesting a bridged Zr-R-Al intermediate (73). A similar reaction can be used to prepare acylaluminum compounds, $(RCO)AlCl_2$, which have potential use in organic synthesis as acyl anion equivalents (74).

Alkenyl groups have also been transferred to Cu or Pd, leading to alkenyl dimers RCH=CH-CH=CHR in high yield (75). Alkenyls undergo conjugate addition to enones in the presence of catalytic amounts of $Ni(acac)_2$, also in high yield and selectivity (76). NiL_4 catalyzes the reaction of (alkenyl)Zr with aryl halides to give the cross-coupling products RCH=CHAr (77).

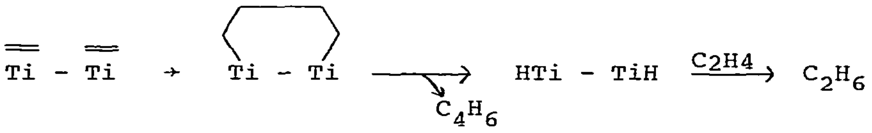
Catalyzed hydrometallations, in which catalytic amounts of group IV metal halides effect addition of aluminum hydrides to olefins, continue to be investigated. The addition of $LiAlH_4$ and other compounds to olefins can be mediated by Cp_2TiCl_2 (78,79), $TiCl_3$ (80), or MCl_4 (M = Ti, Zr) (81). The reaction of Cp_2TiCl_2 with excess $LiAlH_4$ gives a black complex, analyzing as $Cp_2Ti(AlH_3)_2$; this reacts with oct-1-ene to give an orange compound analyzing as the octene adduct, formulated as a π-complex on (somewhat questionable) infrared grounds. The latter reacts with H^+ to give octane and with Br_2 to give 1-bromooctane, suggesting it has a σ-alkyl structure (82). Further work on the Ti-catalyzed alkylation of alkynols, communicated last year, has been described (83).

Many synthetic applications of Ti complexes are known in which the involvement of true organometallics is uncertain. The use of $TiCl_4$ as a synthetic reagent has been reviewed (84). $TiCl_4$ effects carbon-carbon bond formation in ketone silylacetal coupling, leading to substituted succinates (85), and in the photoaddition of methanol to unsaturated compounds (86). Reduced Ti species can be used to make cycloalkenes from diketones $RCO(CH_2)_nCOR$ (87) and to make cyclopropanes from 1,3-diols (88). A mixture of Cp_2TiCl_2 with NaH reduces bromoarenes to arenes (89).

Both $(CpTiH)_2(C_{10}H_8)$ and $Cp_3(\mu\text{-}C_5H_4)Ti_2$ catalyze an unusual transformation of ethylene:

$$3\ C_2H_4 \rightarrow C_2H_6 + \text{1,3-butadiene}$$

A mechanism involving a bimetallocycle was proposed:



$Cp_3(\mu\text{-}C_5H_4)Ti_2$ is much more active than the fulvenide form of titanocene (90). A Cp-Ti-NH_3 complex, prepared by reducing Cp_2TiCl_2 with Li in ammonia, is a hydrogenation catalyst (91).

The hydrogenation of hex-1-ene catalyzed by polymer-supported titanocene was studied as a function of loading. The rate goes through a maximum, indicating an optimum occupancy fraction before inactivating metal-metal interactions become important (92). (Alkoxy-silyl) substituted Cp complexes, such as $(C_5H_4(SiMe_2OEt))CpTiCl_2$, have been prepared and attached to silica to give a different sort of anchored catalyst, which shows greater efficiency than corresponding monomeric species (93).

Arene complexes formed by mixing $TiCl_4$, Al, $AlCl_3$, and arene, plus R_2AlCl, catalyze cyclotrimerization of butadiene and but-2-yne (94). Reduction of $Ti(O\text{-}\underline{t}\text{-}Bu)_4$ with R_3Al gives an isoprene polymerization catalyst which was examined by ESR and chemical ionization mass spectrometry (95). Benzyltitanium compounds also catalyze butadiene and isoprene polymerization; the stereospecifity depends on the catalyst; R_4Ti gives mostly *trans*-1,4 coupling while R_3TiX (X = Cl, Br, I) give increasing amounts of *cis* (96). A review on butadiene polymerization includes a brief section on titanium catalysts (97).

Tetraallylzirconium on silica catalyzes ethylene polymerization; catalytic species were studied by infrared spectroscopy (98). A special preparation of $TiCl_3$ shows enhanced activity for propylene polymerization (99). TiO_2 and ZrO_2 function as cocatalysts in cobalt-catalyzed olefin polymerization (100).

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