TITANIUM, ZIRCONIUM AND HAFNIUM

ANNUAL SURVEY COVERING THE YEAR 1975

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The organometallic chemistry of these metals is receiving an increasing amount of attention. The main emphasis has again been on cyclopentadienyl compounds, although papers on cyclooctatetraenyl and cycloheptatrienyl derivatives feature prominently. Reviews on Organotitanium Compounds (1) and Organohafnium Compounds (2) have been published in Russian.

CRYSTAL STRUCTURES

The structures of seventeen compounds have been investigated by X-ray techniques. Crystal and molecular structures of the titanium(III) complexes, $(Cp_2TiCl)_2 \cdot ZnCl_2 \cdot 2C_6H_6$* and $(Cp_2Ti \cdot DME)_2(Zn_2Cl_6) \cdot C_6H_6$ have been determined from single crystal diffraction data (3). The first contains an approximately linear Ti-Zn-Ti arrangement with double chloride bridges between the metals, while the second shows a tetrahedral cation, $(Cp_2Ti \cdot DME)^+$.

The structures of several cyclopentadienyltitanium(IV) dihalides have been published, including untwinned Cp_2TiCl_2 (4), $(\eta^5\text{-}MeC_5H_4)_2TiCl_2$ (5) and $(\eta^5\text{-}Me_5C_5)_2TiCl_2$ (6). The structural investigation of the MeC_5H_4 derivative formed part of a study by Dahl and collaborators on the nature of the bonding in Cp_2M compounds. The work will be described more fully in the section on Cyclopentadienyl Compounds. In the pentamethyl derivative several ring methyl groups are bent out of the cyclopentadienyl plane away

* Cp = π-cyclopentadienyl

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from the titanium atom. These deviations were attributed to Cl-Me crowding and Me-Me contacts between the two rings.

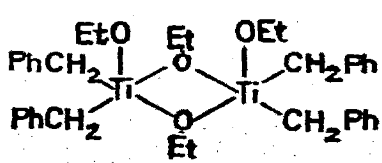
In the tetrahedral dicarbonyl, $Cp_2Ti(CO)_2$ the Ti-CO bond length is 2.030 Å, compared with the average Ti-C(Cp) distance of 2.347 Å (7). Cyclopentadienyltris(tropolonato)zirconium(IV) shows pentagonal bipyramidal geometry with bidentate tropolonato ligands (8).

The crystal structures of the indenyl derivatives, $(\eta^5-C_9H_7)_2MMe_2$, where M = Ti, Zr or Hf, have been determined. The three are isostructural, the indenyl ligands adopting a gauche configuration (9). Cyclooctatetraene derivatives have received attention; cyclooctatetraene titanium chloride is a tetramer, $[(C_8H_8)TiCl]_4$, while the THF adduct is a dimer, $[(C_8H_8)TiCl \cdot THF]_2$ (10). In the zirconium compound, $(C_8H_8)ZrCl_2 \cdot THF$, the zirconium is bonded to each carbon of the COT ligand, to two chlorines and to the O-atom of the THF ligand. The geometry is essentially octahedral, with the COT ligand occupying one face and the remaining three ligands occupying corners of the octahedron (11).

The structure of the first titanacarborane, $[4,4'-Ti-(1,6-C_2B_{10}H_{10}Me_2)_2]^{2-}$ has been investigated (12). It comprises two 13-vertex closed polyhedra fused through the titanium atom, which is sandwiched between roughly parallel six-membered rings.

The structure of bis[tris(diethylamido)titano]ferrocene, $[(Et_2N)_3TiC_5H_4]_2Fe$, predicted earlier (13) has been confirmed (14). A computer drawing of $Hf(BH_4)_4$ from preliminary X-ray data at 24K was presented in a paper discussing the bonding possibilities in $M-BH_4$ compounds (15).

The two titanium atoms of di-μ-ethoxy-bis(dibenzylethoxytitanium) are joined by oxygen bridges. Each titanium atom is pentacoordinate in the form of a distorted trigonal bipyramid (16),



ALKYL AND ARYL DERIVATIVES (Including Allyl)

Insertion of isonitriles, RNC, where R=Me or *t*-Bu, into the halides of titanium, zirconium and hafnium occurs readily, apparently via an intermediate adduct. Multiple insertion may occur for R=Me, but only single insertion for R=*t*-Bu, probably for steric reasons. The compounds obtained, of type $[MCl_3\{C(Cl)=NBu\}(CNBu)]_2$ or $M\{C(Cl)=NMe\}_4$, are poorly soluble and at least dimeric, probably with imino-nitrogen bridges (17).

Trimethylsilylmethyltitanium halides, $(Me_3SiCH_2)_nTiCl_{4-n}$, where n=1 or 2, have been prepared as reddish liquids from $TiCl_4$ and RMgCl or RLi. Thermal stabilities of the alkyls follow the order, $RTiCl_3>R_2TiCl_2>R_4Ti$. The trisalkyl, $(Me_3SiCH_2)_3TiCl$, could not be made in the same way, but was present in mixtures with R_4Ti and R_2TiCl_2. ^1H NMR and infrared data are reported (18).

Standard heats of formation and M-C bond energy terms for d^0 titanium and zirconium compounds, MR_4, where $R=Me_3SiCH_2$, Me_3CCH_2 or $PhCH_2$, have been derived from the heats of alcoholysis of these compounds in isopropyl alcohol, and from subsidiary data. Comparison with alkoxo, amido and halo derivatives showed that for Ti, Zr and Hf, mean bond strengths decreased in the order, M-O>M-Cl>M-N>M-C. The values for zirconium are monotonically higher than those for titanium by 15%, and slightly higher again for hafnium. In neopentyl derivatives a considerably weakened M-C was found (19).

Reaction of $TiCl_4$ with the disilacyclobutane, $Me_2Si(CH_2)_2SiMe_2$, gave a reddish-brown liquid identified from analysis, ^1H NMR and mass spectra as the silylmethyl derivative, $Cl_3TiCH_2Si(Me)_2SiMe_2Cl$ (20).

Tris(π-cyclohexenyl)titanium(III) has been prepared in 10% yield from cyclohexenylmagnesium bromide and $TiCl_4$, as a red-brown paramagnetic solid which decomposed slowly in toluene solution at 23° (21). In a paper by Wilke and coworkers six different types of allylmetal derivatives are distinguished on the basis of infrared and ^1H NMR spectral data;

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viz., π, σ, π and σ-dynamic or static. The spectra of allylzirconium and allylhafnium compounds, MA_4, (COT)MA_2, (COT)M$(Met)_2$, (COT)M$(Crot)_2$, where M = Zr or Hf, A = allyl, Met = methylallyl, Crot = crotyl, COT = cyclooctatetraenyl, are discussed and the compounds classified according to the above scheme. A comprehensive discussion of spectral data and the variation of behaviour with temperature is given (22).

The ionic nature of the lithium alkyltitanium complexes, Li[$TiMe_4R$]·solvent, where R = Cl, Me, Ph or CH_2Ph, has been shown by conductivity measurements in THF and diethyl ether (23).

In connection with olefin polymerizing systems, the reactions between $Ti(CH_2Ph)_4$+$Al(CH_2Ph)_3$, and $Ti(CH_2C_6H_4Me\text{-}p)$+$Al(CH_2C_6H_4Me\text{-}p)$ were investigated using *cryoscopy* as well as ^1H NMR and mass spectroscopy. The extent of the reaction reached a maximum at Al/Ti ratios between 4 and 5, and resulted in elimination of one benzyl ligand as toluene (or *p*-xylene) and reduction of titanium(IV) to titanium(III) in a compound formulated as, $(PhCH_2)_3Ti\underset{Ph}{C}HAl(CH_2Ph)_2$. Dibenzylzinc also reduced $Ti(CH_2Ph)_4$ but the mixture did not polymerize olefins (24). In the polymerization of butadiene, $Ti(CH_2Ph)_4$ and its *o*-chloro and *o*-fluoro analogues showed only slight activity, which was increased somewhat by addition of $AlEt_3$. In the presence of $AlCl_3$, predominantly *cis*-1,4 or *trans*-1,4-polybutadiene was formed (25).

The action of 2 moles of diphenylamine on tetrabenzylzirconium in benzene displaced two benzyl groups and produced yellow, crystalline $(PhCH_2)_2Zr(NPh_2)_2$ in 50% yield (26).

Only one aryl has been reported, $(2,4,6\text{-}Me_3C_6H_2)_4Ti\cdot 2Et_2O$, prepared in 60–70% yield from $TiCl_4$ and RMgBr. Thermolysis at 235^o gave mainly mesitylene, dimesityl, toluene and ethane (27).

CYCLOPENTADIENYL COMPOUNDS

Reduction of Cp_2TiCl_2 with aluminium in THF in the presence of CO has been found to yield $Cp_2Ti(CO)_2$ in 87% yield. The reaction was explained by an equilibrium between the initially formed $(Cp_2TiCl)_2$ and CO,

$$(Cp_2TiCl)_2+2CO \rightleftharpoons Cp_2TiCl_2+Cp_2Ti(CO)_2$$

Zinc and magnesium are also active in this reaction. Reduction of $CpTiCl_3$ with Mg in the presence of cycloheptatriene gave $CpTi(C_7H_7)$ (28). Carbonylation of cyclopentadienyltitanium derivatives to give $Cp_2Ti(CO)_2$ can be facilitated by addition of $AlEt_3$, which increases solubility by complexation. In this way, $Cp_2Ti(CH_2Ph)_2$, Cp_2TiCl_2 and $(Cp_2TiCl)_2$ in heptane were converted to the carbonyl by CO at atmospheric pressure and ambient temperatures. In aromatic solvents secondary reactions during carbonylation led to polymeric compounds containing Ti-O bonds. During the course of this work the new benzyl derivatives, $Cp_2Hf(CH_2Ph)_2$, $(Ind)_2Ti(CH_2Ph)_2$, $(Ind)_2Zr(CH_2Ph)_2$ and $(THInd)_2Ti(CH_2Ph)_2$, where Ind = π-indenyl, and THInd = tetrahydroindenyl, were prepared from $PhCH_2MgCl$ and the appropriate metal halide. The red, crystalline monocarbonyl, $Cp_2Ti(CO)PMe_3$, was also obtained by displacement of one CO from the dicarbonyl with PMe_3. Mention is made of $(Ind)_2Ti(CO)_2$ and $(THInd)_2Ti(CO)_2$ but no details are given (29).

Electrophilic cleavage of the C-Zr bond in alkylzirconium compounds, formed by addition of $Cp_2Zr(Cl)H$ to olefins, has been investigated further. In particular the *erythro-* and *threo-* forms of $Cp_2Zr(Cl)CHDCHDCMe_3$ were cleaved by Br_2 with retention of configuration. The compounds formed by insertion of CO, SO_2 and O between the C and Zr of this alkyl derivative were detected spectroscopically and their NMR parameters tabulated (30).

Terminal or internal olefins can be converted to primary alcohols by oxidation of the alkylzirconium, $Cp_2Zr(Cl)R$, formed by addition of the olefin to $Cp_2Zr(Cl)H$. Protic oxidizing agents such as peroxides and per acids form the alcohol directly, whereas dry oxygen forms initially the alkoxide which must be hydrolyzed (31). With 1,3-dienes the zirconium

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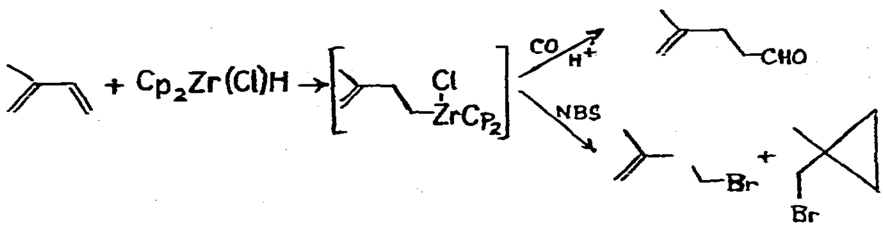
hydride was found to undergo 1,2-addition to the sterically less hindered olefinic unit to give γ,δ-unsaturated complexes in 80-90% yield. Treatment with CO at 20° and 50 psi followed by hydrolysis then gave γ,δ-unsaturated aldehydes, while reaction with N-bromosuccinimide led to bromides, sometimes mixed with the derived cyclopropylcarbinyl bromide (32), e.g.,



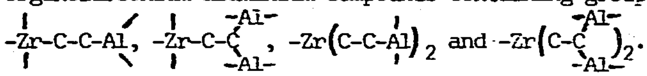
In like manner, addition of $Cp_2Zr(Cl)H$ to acetylenes proceeded stereospecifically *cis* giving vinylzirconium derivatives, e.g., $Cp_2Zr(Cl)C(Me){=}CHEt$ from MeC≡CEt. With N-bromosuccinimide, N-chlorosuccinimide or iodine, vinylic halides could be formed in 53-100% yield with retention of C=C stereochemistry (33).

Triethylgermyl derivatives have received some attention from Russian workers. In tetrahydrofuran, Cp_2TiCl_2 formed a complex with bis(triethylgermyl)cadmium, $Cp_2TiCl_2.Cd(GeEt_3)_2$, which was readily oxidized in air (34). In aromatic solvents slow decomposition occurred at 20°,

$$Cp_2TiCl_2\cdot Cd(GeEt_3)_2 \longrightarrow Cp_2Ti(Cl)GeEt_3 + Cd + Et_3GeCl$$

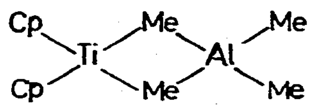
At higher temperatures, reduction of titanium occurred. With $Hg(GeEt_3)_2$ and Cp_2TiCl_2 in benzene, metallic mercury formed immediately together with $(Cp_2TiCl)_2$ and Et_3GeCl. With Cp_2ZrCl_2 in toluene bis(triethylgermyl)cadmium gave $Cp_2Zr(Cl)GeEt_3$ in 41% yield (35).

The meticulous work of Kaminsky and coworkers on the products of the reaction between Cp_2ZrCl_2 and $AlEt_3$ has continued. A range of compounds has been isolated and characterized including $Cp_2Zr(Cl)Et$, and several organozirconium-aluminium compounds containing groups of the type



Preparative procedures are given and the kinetics of their interconversion discussed (36). The [1]H NMR spectra of several of the complexes are detailed in a separate paper (37) with reference to structures, conformation and coalescence temperatures.

The doubly methyl-bridged titanium-aluminium complex,



has been prepared from $(Cp_2TiCl)_2$ and $LiAlMe_4$ in toluene at 0^o. The green, paramagnetic complex decomposed slowly in solution at 0^o. The corresponding yttrium compound was also isolated. Under the same conditions, $NaAlH_2Me_2$ gave the hydrogen-bridged, $Cp_2TiH_2AlMe_2$ (not isolated in a pure state) while Al_2Me_6 formed the 1:1 complex, $Cp_2TiAlMe_3Cl$, the bridging ligands of which could not be identified (38).

The trimetallic titanium(III) species, $(Cp_2TiX)_2MX_2$, where M =Zn, Be or Mn, and X = Cl or Br, have been reinvestigated (3). They were prepared by two general methods; reduction of titanium(IV) species by free metal, or addition of metal halide to a titanium(III) species. The crystalline cyclopentadienyl compounds were solvated, but substitution into the cyclopentadienyl rings allowed solvent-free crystallization. Changes in basicity of solvent can cause dissociation of the trinuclear complexes. Thus in diethyl ether, $(Cp_2TiCl)_2ZnCl_2.2C_6H_6$ dissociated to Cp_2TiCl, whereas in DME the ionic complex, $(Cp_2Ti.DME)_2.(Zn_2Cl_6).C_6H_6$, was formed containing the cation, $[Cp_2Ti(DME)_2TiCp_2]^{2+}$. The benzene molecules in both structures reside in the crystal lattice. X-Ray structural data were mentioned in the first section.

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Attempts to replace the chlorides of $CpTiCl_2$ with two 1-methylallyl groups resulted in the formation of a butadiene complex,

$$\begin{matrix} CpTiCl_2 \\ \text{or} \\ CpTiCl_3 \end{matrix} \xrightarrow{\text{1-MeallylMgBr}} CpTi(h^4\text{-}C_4H_6)(h^3\text{-}C_4H_7)$$

The brown diamagnetic complex was thermally stable (decomposing at 85°C) but sensitive to oxygen. The mode of attachment of the ligands was indicated by the infrared, ^1H NMR, ^{13}C NMR and mass spectra and also by the nature of the products obtained on bromination (39).

Thermal decomposition of bis(cyclopentadienyl)titanium diaryl compounds, Cp_2TiR_2, where R = Ph, 3-MeC_6H_4, 4-MeC_6H_4 or 3,4-$Me_2C_6H_3$, was found to be first order with activation energies of 20-30 kcal $mole^{-1}$, depending on the nature of R. A reaction mechanism was proposed in which the first and rate determining step in the decomposition is the conversion of one of the σ-bonded R ligands to a π-bonded activated state. The effect of deuterated ligands on the activation energies was also studied (40). In a separate paper similar considerations were applied to the benzyl derivative, $Cp_2Ti(CH_2Ph)_2$. Thermal decomposition occurred by abstraction of hydrogen from Cp rings with quantitative formation of toluene. The reaction was first order with an activation energy of 16 kcal $mole^{-1}$ (41).

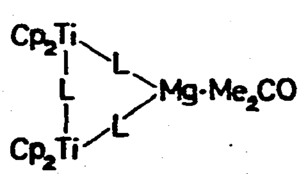
Differential thermal analyses of like compounds, Cp_2TiR_2, where R = H, Me or Ph, have been carried out by other workers (42).

Photolysis under UV light of the cyclopentadienyl and indenyl derivatives, Cp_2TiMe_2 and $(Ind)_2TiMe_2$ in pentane under an atmosphere of CO gave the carbonyls, $Cp_2Ti(CO)_2$ and $(Ind)_2Ti(CO)_2$ in about 50% yield (43).

Diamagnetic Cp_2TiS_5 has been used as a support in a dilute single crystal paramagnetic resonance study of Cp_2VS_5. This work has provided a quantitative determination of the relative metal orbital character and the directional properties of the unpaired electron in paramagnetic Cp_2ML_2 compounds. The results were taken as evidence for the non-validity of the Ballhausen-Dahl model for d^1 and d^2 bis(cyclopentadienyl)metal derivatives, and for the inadequacy of the Alcock model (44). Similar EPR measurements carried out on $(\eta^5\text{-MeC}_5H_4)_2VCl_2$ diluted in $(\eta^5\text{-MeC}_5H_4)_2TiCl_2$ supported the premise that the metal orbital characters of the unpaired electron are not strongly dependent on the nature of the ligands, L. A comparison of X-ray structural data showed that the Cl-Ti-Cl bond angle of 93.2° is 6° larger than the Cl-V-Cl angle, and the Ti-Cl bond length of 2.36Å is 0.04Å shorter than V-Cl. These differences are in harmony with the unpaired electron in the vanadium(IV) complex occupying a molecular orbital which is antibonding with respect to the V-L bonds. Since most of the spin density is localized in the xz plane, a significant interaction with the Cl ligands is possible, from which was rationalized both the decrease in the L-M-L angle and the antibonding effect on the M-L bond as the number of electrons occupying this MO is increased (5).

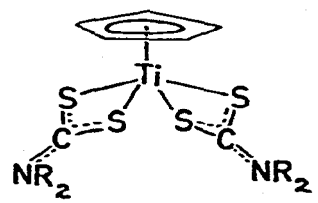
Data from molecular orbital calculations and photoelectron spectra obtained for d^0, d^1 and d^2 titanium and vanadium compounds of type Cp_2ML_2 were found to support the interpretations from the EPR and crystallographic data, that the unpaired electron resides primarily on the metal atom in an a_1-type molecular orbital composed of $3d_{z^2}$ with a small but significant amount of $3d_{x^2-y^2}$ and virtually no 4s character. Photoelectron spectra of Cp_2MCl_2 and $(\eta^5\text{-MeC}_5H_4)_2MCl_2$ were measured and interpreted using approximate molecular orbital calculations (45).

Several organochalcogen derivatives have been prepared. Reaction of Cp_2TiCl_2 with thiosalicylic acid and toluene-3,4-dithiol in the presence of Zn, Mg or Sn, and with ethane-1,2-dithiol in the presence of Zn, gave bimetallic complexes, sometimes solvated with acetone or THF (46); e.g.,

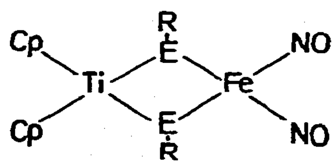


L = thiosalicylato

Ligand exchange reactions between $CpTiCl_2$ and sodium salts of dithiocarbamic acids have given the titanium(III) dithiocarbamates, $CpTi(S_2CNR_2)_2$, where R = Me, Et, Pr and $R_2 = (CH_2)_5$, to which a monomeric five-coordinate structure was assigned (47),



Organochalcogen-bridged binuclear complexes of titanium and iron of type,



have been prepared from $Cp_2Ti(ER)_2$, where ER = SMe, SPh, SeMe, SePh or TePh, and $Hg[Fe(CO)_3NO]_2$ at room temperature in acetone, their rates of formation increasing in the order, E=S<Se<Te. The blue to violet complexes were stable under nitrogen but solutions in DMSO decomposed immediately in air. The ^{1}H NMR spectra showed the presence of isomers, probably *cis*- and *trans*- forms of the ER groups (48).

Mono- and bis(cyclopentadienyl)titanium(III) carboxylates, $[CpTi(O_2CR)_2]_2$ and $Cp_2Ti(O_2CR)$, have been prepared by reduction of the corresponding titanium(IV) tri- and dichlorides with $NaBH_4$ followed by treatment with the appropriate carboxylic acid (49). Spectral and magnetic data agree with those reported earlier. Several triorganosiloxo derivatives of titanium of types, $Cp_2TiCl(OSiRR'_2)$ and $CpTi(OSiRR'_2)_3$, where

R, R' = Me or Ph, have been prepared from the titanium halide and the silanol in the presence of triethylamine, or from the sodium siloxide. Resistance to hydrolysis increased with the number of phenyl groups in the siloxo ligand. Correlations were made between substituents on the silicon and the Cp proton resonances in the PMR spectrum (50).

Titanium-containing carbenoid complexes were made by treatment of $(CO)_5CrC(OLi)X$, where X = NMe_2 or Ph (obtained from $Cr(CO)_6$ and LiX), with Cp_2TiCl_2 in methylene dichloride at -30^o. The carbenoid, $(CO)_5CrC[OTiCp_2Cl]X$, where X = Ph, was more stable than X = NMe_2, which decomposed at room temperature (51). Infrared and electronic structure were reported.

Chemical transformations of the β-diketonates, $CpMR_3$, have been studied, where M = Zr or Hf, R = acetylacetonyl, benzoylacetonyl or dibenzoylmethanyl, and R_3 can be a mixture of these. With HCl or acetic acid, the β-diketonate ligand was replaced more readily than Cp. When R_3 was a mixture of β-diketonate ligands, disproportionation occurred readily (52). With bromine, the Cp ligands were cleaved more readily from both $CpMR_3$ and Cp_2MR_2 giving mainly R_2MBr_2 together with a small amount of Cp_2MBr_2 (53).

Three papers describe amidotitanium derivatives. The reaction of Cp_2TiCl_2 with NaNRR' gave $Cp_2TiCl(NRR')$ and $Cp_2Ti(NRR')_2$, where R, R' = Ph, H; Ph, Ph; $p\text{-}O_2NC_6H_4$, H (54). Displacement of amine from $(R_2N)_4Ti$, where R_2 = Me_2 or C_5H_{10}, by a cyclopentadiene, $C_5H_4R'R''$, where R', R" = H, alkyl, $SiMe_3$ or $GeMe_3$, led to the compounds $(C_5H_3R'R'')Ti(NR_2)_3$, which were mostly red oils. The infrared and Raman spectra were detailed and discussed (55). In a separate comprehensive paper, trends in the ^1H and ^{13}C NMR spectra of these amido compounds were analyzed. As the size of R, R' and R" increased, bending of the rings forced a departure from the h^5 structure of $(R_2N)_3TiCp$ and in the direction of the h^2 structure of $(R_2N)_3Ti(C_5H_3R'R'')$. The indenyl compound, $(Ind)Ti(NMe_2)_3$ probably has a trihapto indenyl ligand (56).

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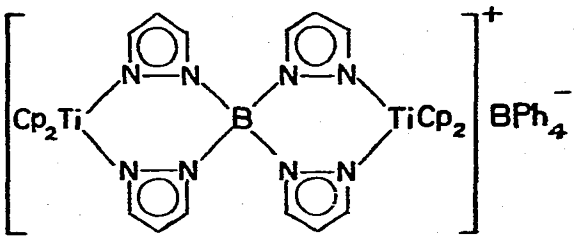
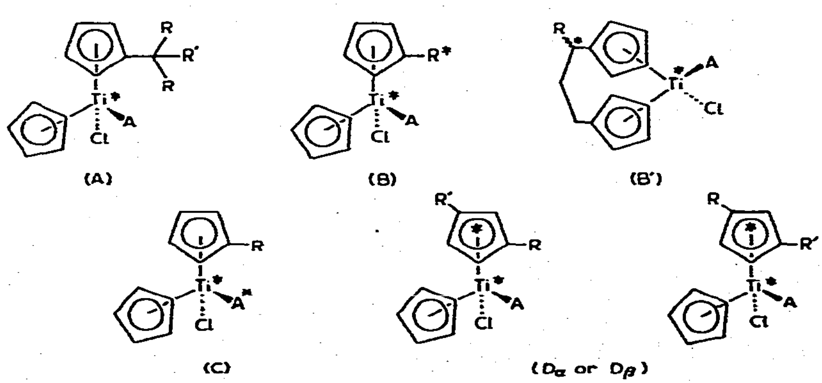
A series of polypyrazolylborate complexes of type, $Cp_2Ti(Pz_{4-x}BH_x)$, where x = 0, 1 or 2: Pz = pyrazolyl or substituted pryazolyl, has been prepared from $(Cp_2TiCl)_2$ with $KHBPz_3$, $KBPz_4$, $KHB(3,5\text{-}Me_2Pz)_3$ and NaH_2BPz_2. The red complex, $CpTiCl_2(HBPz_3)$ from $CpTiCl_3$ and $KHBPz_3$, could be reduced with zinc to $CpTiCl(HBPz_3)$, which was also made from $CpTiCl_2$. The tetrapyrazolylborate complex, Cp_2TiBPz_4, reacted with a further Cp_2TiCl in the presence of $NaBPh_4$ giving the spiro compound (57),



Studies of optical activity in tetrahedral chiral titanium compounds have continued. The full paper describing the various types of activity has been published (58). In some compounds the only chiral element is an asymmetric titanium atom (Type A). A second chiral element can be introduced in three ways:- (i) as an asymmetric carbon atom on a Cp ring (Type B), or as the α-carbon in a trimethylene bridge (Type B'); (ii) as an asymmetric carbon atom in the σ-bonded ligand A (Type C); (iii) if one of the Cp rings carries two different substituents an asymmetric plane is



introduced and two diastereoisomers are possible, corresponding to the two configurations, D_{α} and D_{β}.

Numerous examples are given of the preparation of various members of each class. Their ^{1}H NMR spectra, which allow the detection of chiral characteristics, are discussed. By asymmetric destruction of racemic forms of some of these complexes with mandelic acid, optically active species have been isolated. The syntheses of the substituted cyclopentadienyl compounds from fulvenes have been published in separate papers (59, 60), and the trimethylene-bridged derivatives are also described elsewhere (61). Asymmetric phenoxotitanium derivatives, $Cp_2Ti(OAr)(OAr')$, were obtained by successive or simultaneous replacement of both chlorides of Cp_2TiCl_2 in the presence of base. Mixtures of compounds were obtained including the redistribution products. Selective displacement of OAr ligands by Cl occurred on treatment with HCl, the ease of replacement following the sequence, $OC_6H_4C_6H_5$ > $OC_6H_3Me_2$-2,6 = $OC_6H_2Me_3$-2,4,6 > OC_6H_3Me-3-$CHMe_2$-6 > OC_6H_4Cl-2 (63).

The complex, $CpCp'Ti(Cl)C_6F_5$, where Cp' = π-$C_5H_4CMe_3$, has now been separated into its enantiomeric forms. The racemic form of the compound was converted to the alkoxide, $CpCp'Ti(C_6F_5)OCH_2CH(Me)Ph$, which was separated into its diastereoisomers by TLC. By the action of HCl in benzene each diastereoisomer was converted stereospecifically to the corresponding enantiomer of $CpCp'Ti(Cl)C_6F_5$ (64).

Complexes of Type A of general formula, CpCp'Zr(Cl)R, where Cp' = π-$C_5H_4CHMe_2$ and R = OC_6H_{11}, OCH_2Ph or CH_2Ph, have now been made with zirconium compounds (65).

Several papers describe physical measurements carried out on known compounds. Variable temperature ^{1}H NMR studies of $Cp_2Zr(BH_4)_2$, $Cp_2Hf(BH_4)_2$ and $Cp_2Zr(H)BH_4$ indicated rapid exchange of C_5H_5 and BH_4 protons. With increasing temperature, resonances due to both types of ligand protons broadened in a manner consistent with exchange between two nearly equally

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populated sites. The invariant nature of the lines on dilution was taken as evidence for an intramolecular exchange. Free energies of activation were calculated and possible mechanisms discussed (66).

Exchange of Cp ligands between $(Cp_2TiCl)_2$ and $[(d_5\text{-}Cp)_2TiCl]_2$, has been observed in benzene under photolysis at 313 nm. The rates of exchange were monitored by mass spectral measurements (67). The He(I) photoelectron spectra of Cp_2MCl_2, where M = Ti, Zr or Hf, have been measured. The spectral bands are mainly due to ionization of electrons localized on the cyclopentadienyl ligands. The one-electron transition energies from MO calculations agree well with the experimental band maxima (68).

The system, Cp_2TiCl_2 + Mg, has been found useful for the reduction of organic halides to alkanes. Both alkyl and aryl halides are reduced in good yield at 0^o. Deuteration experiments indicated that the reducing hydrogen originated from the Cp ligands. Azo compounds, α-haloketones and α-haloesters are also reduced (69).

In a paper in memory of Professor Ziegler, the effect of adding small quantities of water to the system, Cp_2TiCl_2 + Me_2AlCl, is described. An active catalyst for olefin polymerization was produced. Neither oxygen nor alcohols had the same effect (70). The photoinduced polymerization of styrene in the presence of the titanium compounds, $TiCl_4$, $Ti(CH_2Ph)_4$, Cp_2TiCl_2, $Cp_2Ti(Cl)C_2H_5$ and $Cp_2Ti(Cl)CPh_3$ has been investigated. In the case of those compounds with a Ti-C bond, polymerization occurs by a radical mechanism (71). Cyclopentadienyltitanium compounds attached to styrene-divinylbenzene copolymers through the Cp ring have been prepared. After reduction with BuLi or $Na/C_{10}H_8$, the complexes showed enhanced effectiveness as olefin hydrogenation catalysts (72).

OTHER π-BONDED COMPLEXES.

A series of ring-substituted sandwich complexes, $CpTi(h^7\text{-}C_7H_6Ph)$,

$CpTi(h^7-C_9H_9)$ and $(h^5-R)Ti(h^7-C_7H_7)$, where R = $C_5H_4CMe_3$, $C_5H_4SiMe_3$ or indenyl, has been synthesized. Their infrared, NMR and mass spectra were measured and discussed. The compounds were made from $CpTiCl_3$ (or $h^5-RTiCl_3$), treated with iso-C_3H_7MgBr in the presence of excess C_7H_7R, or with 3 moles of cyclononatetraenyllithium (73). As mentioned in the previous section, magnesium metal is also a satisfactory reducing agent for the preparation of $CpTi(C_7H_7)$ (28).

A synthesis of cyclooctatetraenetitanium chloride, $(C_8H_8)TiCl.THF$, has been reported from $TiCl_3$ and $K_2C_8H_8$ in THF. Adducts of type $(C_8H_8)TiCl.L$, where L = Et_2NH, pyrrolidine or pyridine, were obtained by displacement of THF by L. The uncomplexed compound, $(C_8H_8)TiCl$, could be isolated by repeated washing of the THF adduct with ether. Single crystal X-ray structure determination showed the uncomplexed derivative to be a tetramer, while the THF adduct is a dimer (10). Treatment of $(C_8H_8)TiCl.THF$ with RMgX, where R = allyl, 1- and 2-methylallyl; X = Cl or Br, in ether gave the allyl derivatives, $(h^8-C_8H_8)Ti(h^3-R)$, while in THF $(h^8-C_8H_8)Ti(h^3-R).THF$ were obtained. The paramagnetic compounds were sensitive to air and water and decomposed slowly at room temperature (74).

Addition of iodine to $CpTi(C_8H_8)$ in ether gave the monoiodide, $Cp(C_8H_8)TiI$, or the triiodide, $Cp(C_8H_8)TiI_3$, depending on stoichiometry. The iodides were stable to air but not to water, and treatment with LiPh or KCNS removed the iodide ions leaving the original compound. The lack of parent peaks in the mass spectra of the iodides was taken as indication of the ionic nature of the compounds and highlighted the extreme lability of the iodide ions (75). Metallation of $CpTi(C_8H_8)$ with LiBu was more difficult than $CpTi(C_7H_7)$, and in contrast to the latter compound, took place on the C_5 ring. Qualitative molecular orbital considerations indicated a smaller polarity of $CpTi(C_8H_8)$ compared with $CpTi(C_7H_7)$, which was reflected in the dipole moment and the positive charge on the metal

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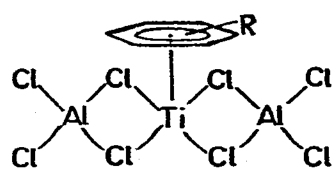
as shown by ESCA. The C_8H_8 ring appears to be virtually neutral whereas the C_7H_7 ring carries a charge equivalent to 0.7-0.8 electrons (76).

The He(I) photoelectron spectrum of $CpZr(C_7H_7)$ has been measured and compared with those of the corresponding niobium and molybdenum derivatives and with the 3d analogues. Molecular orbital considerations are discussed (77).

Simultaneous addition of $K_2C_8H_8$ and NaC_9H_7 to $TiCl_4$ in benzene or toluene gave a green solution from which indenylcyclooctatetraenyltitanium(III) was isolated. The poorly soluble compound could be sublimed at $130^0/10^{-4}$mm, and was sensitive to water and to oxygen. Comparison with $CpTi(C_8H_8)$ and analysis of the infrared spectrum gave evidence of the aromatic character of the indenyl and cyclooctatetraenyl ligands and of the sandwich structure of the compound (78). Electronic configurations have been proposed for dicyclooctatetraenyltitanium and vanadium complexes on the basis of group theory considerations of symmetry and molecular orbitals (79).

In a series of arenetitanium(II) complexes of type,



prepared from $TiCl_4$ + Al + $AlCl_3$ + arene, stability was found to increase in the order, benzene < toluene < xylene < mesitylene < durene < hexamethylbenzene. So much so that the last two were best made by displacement of benzene from $C_6H_6 \cdot TiCl_2 Al_2Cl_6$. With increasing methyl substitution of the aromatic ring the conductivity in benzene also increased at a rate inversely proportional to the ionization potential of the arene. The ^{1}H NMR spectrum of the hexamethylbenzene derivative could be measured but the lower members of the series are paramagnetic (80).

The preparation of the di(η-arene)titanium complexes, $(C_6H_6)_2Ti$, $(MeC_6H_5)_2Ti$ and $(mes)_2Ti$, where mes = mesitylene, has been described. The arene is cocondensed with metal atoms generated in a metal vapourization apparatus. Symmetrical sandwich structures for the complexes are proposed on the basis of ^{1}H NMR, infrared, mass and photoelectron spectroscopy (81). The full paper on the catalytic oligomerization of butadiene using catalysts derived directly from metal atoms or di(η-arene)titanium compounds has been published (82). Titanium atoms alone do not cause polymerization but in the presence of alkylaluminium halides, cyclododecatriene isomers resulted. The predominance of the *c*, *t*, *t*-isomer over the *t*, *t*, *t*-isomer in this reaction was reversed in the presence of PPh_3.

The dianions generated from the *closo*-carboranes, 1,2-$C_2R_2B_{10}H_{10}$, where R = H or Me, have been shown to react with $TiCl_4$, $ZrCl_4$ and VCl_3 to give a series of anionic metallocarboranes formulated as $[M(C_2R_2B_{10}H_{10})_2]^{2-}$, with M in the formal +2 oxidation state and isolable in good yields as tetraalkylammonium salts. The orange to red titanium derivatives were moderately stable in air but the purple zirconium complex (R = Me) decomposed completely in air in 20 minutes. Both the ^{11}B and ^{1}H NMR data indicated fluxionality in solution (83). The crystal and molecular structure of the methyl derivative, $[4,4'\text{-Ti-}(1,6\text{-}C_2B_{10}H_{10}Me_2)_2]^{2-}$ has been determined (12) (see Crystal Structures and structure A below).

Mixed ligand titanacarboranes have been isolated from the reaction between $CpTiCl_2$ or $CpTiCl_3$ and $Na_2C_2B_{10}H_{12}$. After treatment with zinc dust the complex, $[4\text{-Cp-}4,1,6\text{-}TiC_2B_{10}H_{12}]^-$ was isolated as the red tetraethylammonium salt, containing titanium in the +2 oxidation state. Similarly from $(C_8H_8)TiCl$ and $Na_2C_2B_9H_{11}$ in THF, the air-sensitive, paramagnetic, $[Et_4N][3\text{-}(\eta^8\text{-}C_8H_8)\text{-}3,1,2\text{-}TiC_2B_9H_{11}]$ was isolated.

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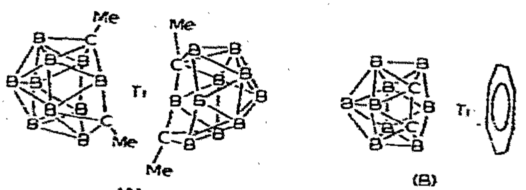
Oxidation with H_2O_2 led to neutral 3-(η^8-C_8H_8)-3,1,2-$TiC_2B_9H_{11}$, with proposed structure B, stable in air to 300°C (84).



(A) (B)

REFERENCES

1. O.V. Nogina, *Metody Elem.-Org. Khim.*, 1 (1974) 145.
2. E.M. Brainina, *Metody Elem.-Org. Khim.*, 1 (1974) 373.
3. D.G. Sekutowski and G.D. Stucky, *Inorg. Chem.*, 14 (1975) 2192.
4. A. Clearfield, D.K. Warner, C.H. Saldarriaga-Molina and R.Ropal, *Can. J. Chem.*, 53 (1975) 1622.
5. J.L. Petersen and L.F. Dahl, *J. Amer. Chem.Soc.*, 97 (1975) 6422.
6. T.C. McKenzie, R.D. Sanner and J.E. Bercaw, *J. Organometal. Chem.*, 102 (1975) 457.
7. J.L. Atwood, K.E. Stone, H.G. Alt, D.C. Hrncir and M.D. Rausch, *J. Organometal. Chem.*, 96 (1975) C4.
8. M. McPartlin and J.C. Matthews, *J. Organometal. Chem.*, 104 (1976) C20.
9. J.L. Atwood, W.E. Hunter, D.C. Hrncir, E. Samuel, H. Alt and M.D. Rausch, *Inorg. Chem.*, 14 (1975) 1757.
10. H.R. van der Wal, F. Overzet, H.O. van Oven, J.L. de Boer, H.J. de Liefde Meijer and F. Jellinek, *J. Organometal. Chem.*, 92 (1975) 329.
11. D.J. Brauer and C. Krüger, *Inorg. Chem.*, 14 (1975) 3053.
12. F.Y. Lo, C.E. Strouse, K.P. Callahan, C.B. Knobler and M.F. Hawthorne, *J. Amer. Chem. Soc.*, 97, (1975) 428.

13. H. Bürger and C. Kluess, *J. Organometal. Chem.*, 56 (1973) 269

14. U. Thewalt and D. Schomburg, *Z. Naturforsch.*, 30b (1975) 636.

15. T.A. Keiderling, W.T. Wozniak, R.S. Gay, D. Jurkowitz, E.R. Bernstein, S.J. Lippard and T.G. Spiro, *Inorg. Chem.*, 14 (1975) 576.

16. H. Stoeckli-Evans, *Helv. Chim. Acta*, 58 (1975) 373.

17. B. Crociani, M. Nicolini and R.L. Richards, *J. Organometal. Chem.*, 101 (1975) C1.

18. S.I. Beilin, G.N. Bondarenko, V.M. Vdovin, B.A. Dolgoplosk, I.N. Markevich, N.S. Nametkin, V.A. Poletaev, V.I. Svergun and M.B. Sergeeva, *Dokl. Akad. Nauk SSSR*, 218 (1974) 1347.

19. M.F. Lappert, D.S. Patil and J.B. Pedley, *J. Chem. Soc., Chem. Commun.*, (1975) 830.

20. N.S. Nametkin, V.M. Vdovin, V.A. Potetaev, V.I. Svergun and M.B. Seryeeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1974) 2861.

21. S.I. Beilin, I.N. Markevich, S.B. Gol'shtein, G.N. Bondarenko and B.A. Dolgoplosk, *Dokl. Akad. Nauk SSSR*, 218 (1974) 837.

22. E.G. Hoffmann, R. Kallweit, G.Schroth, K. Seevogel, W. Stempfle and G. Wilke, *J. Organometal Chem.*, 97 (1975) 183.

23. H. Rau and J. Müller, *Z. Anorg. Allg. Chem.*, 415 (1975) 225.

24. P. Pino, G. Consiglio and H.J. Ringger, *Ann. Chem.*, (1975) 509.

25. F. Brune, K.H. Thiele and Th. Schoeneburg, *J. Prakt. Chem.*, 317 (1975) 143.

26. H-O Fröhlich and S. Keiser, *Z. Chem.*, 15 (1975) 30.

27. G.A. Razuvaev, V.N. Latyaeva, G.A. Kilyakova and V.P. Mar'in, *Tr. Khim. Khim. Tekhnol.*, (1974) 35; *Chem. Abs.*, 83 (1975) 179262.

28. B. Demerseman, G. Bouquet and M. Bigorgne, *J. Organometal. Chem.*, 101 (1975) C24.

29. B. Demerseman, G. Bouquet and M. Bigorgne, *J. Organometal. Chem.*, 93 (1975) 199.

30. J.A. Labinger, D.W. Hart, W.E. Seibert and J. Schwartz, *J. Amer. Chem. Soc.*, 97 (1975) 3851.

31. T.F. Blackburn, J.A. Labinger and J. Schwartz, *Tetrahedron Lett.* (1975) 3041.

32. C.A. Bertelo and J. Schwartz, *J. Amer. Chem. Soc.*, 98 (1976) 262.

33. D.W. Hart, T.F. Blackburn and J. Schwartz, *J. Amer. Chem. Soc.*, 97 (1975) 679.

34. G.A. Razuvaev, V.N. Latyaeva, L.I. Vishinskaya, V.T. Bytchkov and G.A. Vasilyeva, *J. Organometal. Chem.*, 87 (1975) 93.

35. V.T. Bytchkov, I.V. Lomakova and G.A. Domrachev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1975) 2115.

36. W. Kaminsky and H. Sinn, *Ann. Chem.*, (1975) 424.

37. W. Kaminsky and H.-J. Vollmer, *Ann. Chem.*, (1975) 438.

38. D.G.H. Ballard and R. Pearce, *J. Chem. Soc., Chem. Commun.*, (1975) 621.

39. A Zwijnenburg, H.O. van Oven, C.J. Groenenboom and H.J. de Liefde Meijer, *J. Organometal. Chem.*, 94 (1975) 23.

40. C.P. Boekel, J.H. Teuben and H.J. de Liefde Meijer, *J. Organometal. Chem.*, 102 (1975) 161.

41. C.P. Boekel, J.H. Teuben and H.J. de Liefde Meijer, *J. Organometal. Chem.*, 102 (1975) 317.

42. G.A. Razuvaev, L.I. Vyshinskaya, V.P. Mar'in and V.I. Khruleva, *Dokl. Akad. Nauk SSSR*, 225 (1975) 827.

43. H.G. Alt and M.D. Rausch, *Z. Naturforsch.*, 30b (1975) 813.

44. J.L. Petersen and L.F. Dahl, *J.Amer. Chem. Soc.*, 97 (1975) 6416.

45. J.L. Petersen, D.L. Lichtenberger, R.F. Fenske and L.F. Dahl, *J. Amer. Chem. Soc.*, 97 (1975) 6433.

46. D.N. Sen and U.N. Kantak, *Indian J. Chem.*, 13 (1975) 72.

47. R.S.P. Coutts and P.C. Wailes, *Aust. J. Chem.*, 27 (1974) 2483.

48. M. Sato and T. Yoshida, *J. Organometal. Chem.*, 94 (1975) 403.

49. A.A. Pasynskii, T. Ch. Idrisov, K.M. Suvorova, I.L. Eremenko, E.B. Ivanova and V.T. Kalinnikov, *Izv. Akad. Nauk SSR, Ser. Khim.*, (1974) 2564

50. H. Suzuki and T. Takiguchi, *Bull. Chem. Soc. Jap.*, 48 (1975) 2460.

51. H.G. Raubenheimer and E.O. Fischer, *J. Organometal. Chem.*, 91 (1975) C23.

52. E.M. Brainina and M. Kh. Minacheva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1974) 2093.

53. E.M. Brainina and M. Kh. Minacheva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1975) 1596.

54. L.J. Baye, *Synth. React. Inorg. Met.-Org. Chem.*, 5 (1975) 95.

55. H. Bürger and U. Dämmgen, *J. Organometal. Chem.*, 101 (1975) 295.

56. U. Dämmgen and H. Bürger, *J. Organometal. Chem.*, 101 (1975) 307.

57. L.E. Manzer, *J. Organometal. Chem.*, 102 (1975) 167.

58. A. Dormond, J. Tirouflet and F. Le Moigne, *J. Organometal. Chem.*, 101 (1975) 71.

59. A. Dormond, Ou-Khan and J. Tirouflet, *C. R. Hebd. Seances Acad. Sci., Ser. C,* 280 (1975) 389.

60. J. Besancon, S. Top and J. Tirouflet, *C.R. Hebd. Seances Acad. Sci., Ser. C,* 281 (1975) 135.

61. A. Dormond, J.P. Letourneux and J. Tirouflet, *C.R. Hebd. Seances Acad. Sci., Ser. C,* 280 (1975) 477.

62. M.L. Martin, J. Tirouflet and B. Gautheron, *J. Organometal. Chem.*, 97 (1975) 261.

63. J. Besancon, F. Huq and M. Colette, *J. Organometal. Chem.*, 96 (1975) 63.

64. C. Moise, J.C. Leblanc and J. Tirouflet, *J. Amer. Chem. Soc.*, 97 (1975) 6272.

65. G. Tainturier, B. Gautheron, P. Renaut and P. Etiévant, *C.R. Hebd. Seances Acad. Sci., Ser. C,* 281 (1975) 1035.

66. T.J. Marks and J.R. Kolb, *J. Amer. Chem. Soc.*, 97 (1975) 3397.

67. E. Vitz and C.H. Brubaker, *J. Organometal. Chem.*, 104 (1976) C33.

68. G. Condorelli, I. Fragala, A. Centineo and E. Tondello, *J. Organometal. Chem.*, 87 (1975) 311.

69. T.R. Nelson and J.J. Tufariello, *J. Org. Chem.*, 40 (1975) 3159.

70. W.P. Long and D.S. Breslow, *Ann. Chem.*, (1975) 463.

71. T.S. Dzhabiev, F.S. D'yachkovskii and L.I. Chernaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1975) 1091.

72. W.D. Bonds, C.H. Brubaker, E.S. Chandrasekaran, C. Gibbons, R.H. Grubbs and L.C. Kroll, *J. Amer. Chem. Soc.*, 97 (1975) 2128.

73. H.T. Verkouw, M.E.E. Veldman, C.J. Groenenboom, H.O. van Oven and H.J. de Liefde Meijer, *J. Organometal. Chem.* 102 (1975) 49.

74. H.K. Hofstee, C.J. Groenenboom, H.O. van Oven and H.J. de Liefde Meijer, *J. Organometal. Chem.*, 85 (1975) 193.

75. J. Knol, A. Westerhof, H.O. van Oven and H.J. de Liefde Meijer, *J. Organometal. Chem.*, 96 (1975) 257.

76. M. Vlick, C.J. Groenenboom, H.J. de Liefde Meijer and F. Jellinek, *J. Organometal. Chem.*, 97 (1975) 67.

77. C.J. Groenenboom, H.J. de Liefde Meijer, F. Jellinek and A. Oskam, *J. Organometal. Chem.*, 97 (1975) 73.

78. J. Goffart and G. Duyckaerts, *J. Organometal. Chem.*, 94 (1975) 29.

79. L. Hocks, R. Hubin and J. Goffart, *J. Organometal. Chem.*, 104 (1976) 199.

80. R. Giezynski, S. Dzierzgowski and S. Pasynkiewicz, *J. Organometal. Chem.*, 87 (1975) 295.

81. M.T. Anthony, M.L.H. Green and D. Young, *J. Chem. Soc., Dalton Trans.*, (1975) 1419.

82. V.M. Akhmedov, M.T. Anthony, M.L.H. Green and D. Young, *J. Chem. Soc., Dalton Trans.*, (1975) 1412.

83. C.G. Salentine and M.F. Hawthorne, *J. Amer. Chem. Soc.*, 97 (1975) 426.

84. C.G. Salentine and M.F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, (1975) 848.