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TITANIUM, ZIRCONIUM AND HAFNIUM
ANNUAL SURVEY COVERING THE YEAR 1978

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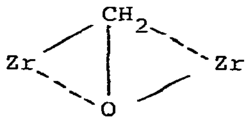
This survey is organized by ligand type, with complexes containing more than one class of ligand listed according to the feature of primary interest. The abbreviations Cp (for η^5-cyclopentadienyl) and Cp' (for any ring-substituted cyclopentadienyl group) are used throughout.

It is notable that in both this survey and the accompanying one on group V, the number of papers which appeared this year increased by fully one-third over the year before.

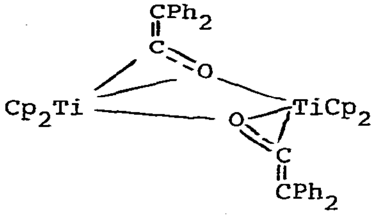
CARBONYL AND DINITROGEN COMPLEXES

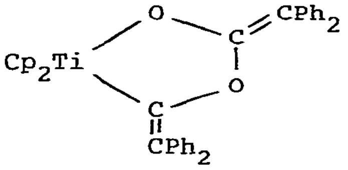
Still another example of CO hydrogenation has been reported. A suspension of Cp_2ZrHCl absorbs 0.5 mol CO to give a product characterized as $Cp_2ClZr-CH_2-O-ZrClCp_2$: e.g., reaction with D_2O gives CDH_2OH. The ^1H NMR shows a single Cp peak, suggesting a side-on orientation for the bridging unit allowing facile interchange of the two Zr centers:



With excess CO_2, Cp_2ZrHCl gives $(Cp_2ZrCl)_2O$ plus formaldehyde; the latter reacts with more Cp_2ZrHCl to form $Cp_2ZrCl(OCH_3)$ (1). A full paper reports further details on the reduction of CO by $(C_5Me_5)_2ZrH_2$, communicated in 1976 (2). (This paper also reports on reactions of Zr alkyls with CO, which will be discussed in the following section.) Reaction of Cp_2TiCl_2 with Al (or Zn) and CO_2 gives $Cp_2Ti(CO)_2$ plus Ti(III) carbonate complexes; formation of the former is improved by Lewis acids such as $AlCl_3$ (3).

The reaction of $Cp_2Ti(CO)_2$ with diphenyl ketene is reported in both a communication (4) and full paper (5). An equimolar mixture gives $[Cp_2Ti(Ph_2C{=}C{=}O)]_2$ which is converted by excess ketene (reversibly) to $Cp_2Ti(Ph_2C{=}C{=}O)_2$; X-ray crystal structures show the following units:



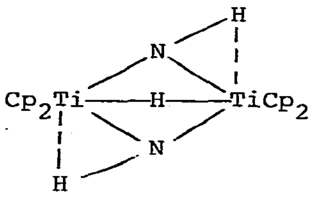


It is noteworthy that $Ph_2C{=}C{=}O$ coordinates to Ti (in the dimer) in a η^2-C=O mode, whereas with later transition metals (e.g. Mn) it coordinates through the C=C double bond. Acid cleavage of the dimer gives CO plus hydrocarbons, Ph_2CH_2 and $(Ph_2CH)_2$.

Several review articles cover N_2 chemistry in this group: a general review on nitrogen fixation (6); a review of metal halide-Mg-N_2 systems (7); and an account of $(C_5Me_5)_2$-Ti or Zr-N_2 chemistry (8). A full paper on NMR studies of $[(C_5Me_5)_2ZrN_2]_2N_2$ and related compounds has appeared; ^{15}N NMR shows the terminal dinitrogen ligands are labile to dissociation but the bridging one is not (9).

Reduction of $Cp_2ZrCl(CH(SiMe_3)_2)$ by sodium amalgam under N_2 gives brown, paramagnetic $Cp_2ZrR(N_2)$. The ESR (equivalent hyperfine coupling to both N nuclei) and IR (no assignable N-N stretch) spectra suggest the possibility of a side-on bonded N_2 ligand. On heating, the Zr(III) complex is converted to purple, diamagnetic $(Cp_2ZrR)_2N_2$, while acidification gives small amounts of N_2H_4 and NH_3 (10). Sodium amalgam reduces $TiCl_2(OPh)_2$ under N_2 to a compound analyzing as $[Ti(OPh)_2]_2N_2H_2$; the IR spectrum gave no clear indication of the structure although a bridging N_2 seems likely (11). Reduction of Cp_2TiPh_2 by metallic Li, Na or Mg under N_2, followed by hydrolysis, gives up to 18% $PhNH_2$ per Ti plus NH_3 (12).

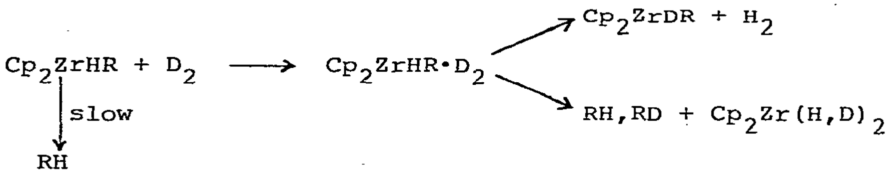
The reactive form of titanocene, $Cp_3(C_5H_4)Ti_2$, reacts with NH_3 to give a complex analyzing as $(Cp_2Ti)_2N_2H_3$. The compound is paramagnetic (μ = 1.9 B.M.; ESR at g = 1.979), with one unpaired electron per Ti_2 unit. An X-ray structure failed to locate the hydrogens, but showed two Cp_2Ti units bridged by two N atoms and separated by 3.392 Å; based on IR and chemical evidence (e.g., MeI reacts to give only one equivalent of CH_4) the following structure was proposed:



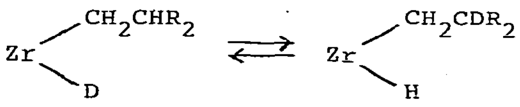
Substituted amines undergo analogous reactions but much more slowly (13). The compound forms a reversible N_2 adduct, which on reduction and protonolysis gives 80% NH_3; it also reacts with CO to give a compound believed to contain a Ti-NCO unit (plus $Cp_2Ti(CO)_2$) and catalyzes olefin hydrogenation. With C_2H_4 plus NH_3, small amounts of ethylamines were obtained (14).

ALKYL AND ARYL COMPLEXES

This section shows the largest expansion over last year, with studies on decomposition modes continuing to attract considerable attention. Results concerning reductive elimination from hydrido-alkyl Zr(IV) complexes are of particular interest. Cp_2ZrRCl can be reduced to Cp_2ZrRH, which appears to exist as a partly dissociated dimer in solution. By itself it slowly decomposes to RH; however, under H_2 the formation of RH is much faster and first order in $[H_2]$. Labelling studies show that the Zr-H exchanges with D_2 even faster than reductive elimination, implying the following scheme:

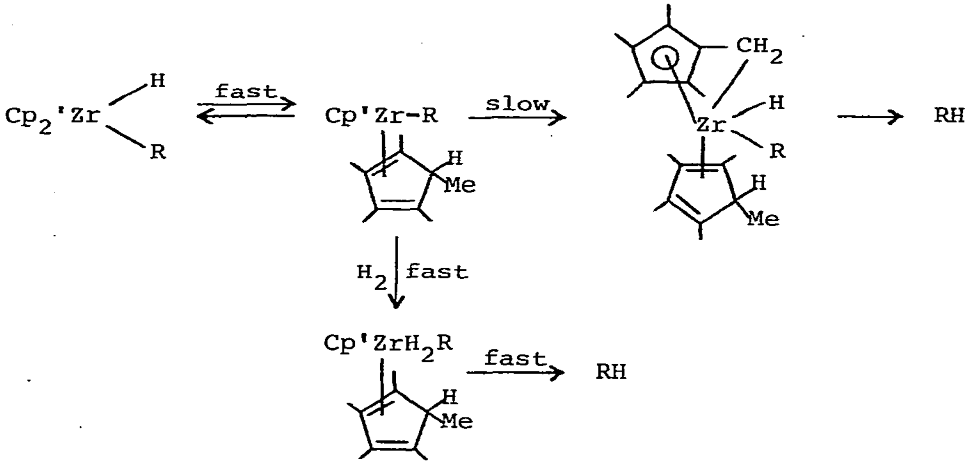


The nature of the intermediate is unclear; considering it as a normal oxidative adduct is unattractive, requiring a formal oxidation state of +6. Instead it was suggested that H_2 acts as a two-electron donor to the d^0, Zr(IV) complex. Intramolecular exchange is also observed, viz:



presumably via an olefin intermediate (15).

The behavior of the C_5Me_5 analogs is strikingly different. Reaction of $Cp_2'ZrH_2$ with isobutylene gives $Cp_2'ZrH(iBu)$, which yields isobutane slowly at 75° or rapidly under H_2 at -15°, similar to the ordinary Cp system. However, the results of labelling experiments are surprising: $Cp_2'ZrD(CH_2CDMe_2)$ gives CH_3CDMe_2, while $(C_5(CD_3)_5)_2ZrD(CH_2CDMe_2)$ gives CH_2DCDMe_2, indicating involvement of the Cp' rings. Under H_2 the latter compound gives CH_3CDMe_2 but does not show rapid exchange of the Zr-D. The following mechanism was proposed to account for these findings (16):

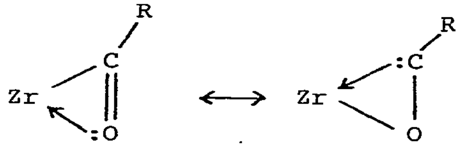


It should be noted that there is nothing necessarily contradictory between these two sets of results. In fact, it is entirely reasonable that this mechanism, which begins with a step which should tend to relieve steric crowding, would be more favorable with the much bulkier C_5Me_5 ligand; whereas the increased crowding on adding an additional molecule of H_2 would be strongly disfavored for C_5Me_5. It does not appear that the cyclopentadiene intermediate can be a major route in the C_5H_5 system, since it would not account for the facile H-D exchange observed. This seems thus to be another example of a surprisingly common phenomenon in organotransition metal chemistry: two closely similar systems undergoing stoichiometrically identical reactions by quite different mechanisms.

In both systems, reductive elimination can be accelerated by other ligands as well; e.g., $Cp_2'ZrHR + C_2H_4 \rightarrow RH + Cp_2'Zr(CH_2)_4$ (16); $Cp_2ZrHR + R'C\equiv CR' \rightarrow RH + Cp_2Zr(CR')_4$. In the latter case, $Cp_2ZrD(C_7H_{12}D)$ gives $C_7H_{12}D_2$ cleanly with alkyne present, whereas the slower non-induced reductive elimination gives a mixture of d_o, d_1 and d_2 products (17). CO also induces reductive elimination from

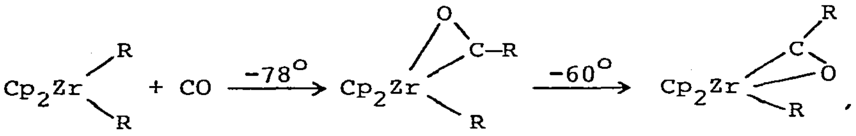
Cp_2ZrHR, but in this case there is a competing reaction: after hydrolysis, RCH_2OH (major), RCHO and $RCOCH_2OH$ (trace, but can be made major product at high CO pressure) are formed; the added carbons were shown by ^{13}C labelling to come from CO. The mechanism proposed involves an insertion step to give $Cp_2ZrH(COR)$ followed by intermolecular attack on the acyl by Cp_2ZrHR, leading to a hydroxyalkyl equivalent, $Cp_2HZr(OCHR)ZrRCp_2$, which would give alcohol on hydrolysis or, with high [CO], insert another CO leading to the hydroxy ketone. It was independently found that $Cp_2ZrCl(COR)$ is attacked by Cp_2ZrHCl to give the analog of the postulated intermediate, $(Cp_2ClZr)_2(\mu\text{-}OCHR)$ (18). (The close connection between these results and the work on Cp_2ZrHCl plus CO, vide supra, should be noted.)

Again, the behavior of the C_5Me_5 system is very different. $Cp_2'ZrH(i\text{-}Bu)$ adds CO at 25° to give $Cp_2'ZrH(OCH{=}CHCHMe_2)$; at -50°, the expected intermediate acyl, $Cp_2'ZrH(COCH_2CHMe_2)$ can be observed. The labelling pattern is again interesting: $Cp_2'ZrD(CH_2CDMe_2)$ gives $Cp_2'ZrH(OCD{=}CHCDMe_2)$. The explanation offered is based on the fact that the acyl group in such complexes is side-on bonded (cf. surveys for last two years); such a structure might have some carbenoid character:



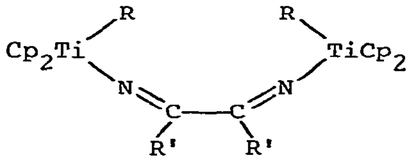
Insertion of the carbene into the Zr-H bond followed by β-hydrogen elimination from the resulting aldehyde would give the alkenoxide with the observed labelling pattern. Other reaction products which may be similarly explained include: $Cp_2'ZrMe_2 + CO \xrightarrow{75^\circ} Cp_2Zr(OCMe{=}CMeO)$ and $Cp_2'ZrH_2 + CO \longrightarrow (Cp_2ZrH)_2(OCH{=}CHO)$ (by dimerization of the carbenoid groups); and $Cp_2'Zr(CH_2)_4 + CO \longrightarrow Cp_2'ZrH$(cyclopent-1-enolato) (2).

The reaction of Cp_2ZrR_2 (R=Ph, p-tolyl) with CO at -78° gives a compound similar but not identical to the room temperature product; it was proposed that it is an isomeric form:



This appears to suggest that CO preferentially coordinates outside the R groups (19). (Note however that the NMR of $Cp_2'ZrH_2(CO)$ at low temperature shows equivalent coupling to both hydrogens (2).)

The nature of the dimeric products from Cp_2TiR plus R'CN, communicated last year, has now been elucidated:



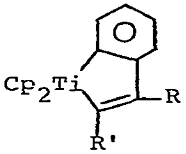
It was proposed that the initial Ti(III) adducts, $Cp_2TiR(R'CN)$, have some unpaired electron density on the nitrile carbon, allowing direct coupling (20).

Protonolysis of $TiMe_4$ by RCOOH gives $Ti(O_2CR)_4$ for $R=CH_3$ but $Ti(O_2CR)_3$ for $R=CF_3$ (21). A metal-alkyl bond in Cp_2ZrMe_2 can be cleaved by very weakly acidic $CpMo(CO)_3H$, leading to metal-metal bonded $Cp_2MeZr-Mo(CO)_3Cp$; the Zr-Mo bond is cleaved by CCl_4 or HCl (22).

The formation of ethylene from $Cp_2Ti(CH_2)_4$ has been previously reported; it is found that if $Cp_2Ti(CD_2CH_2CH_2CD_2)$ is prepared and allowed to stand before cleaving with HCl or Br_2, increasing amounts of 1,1,3,3- and 2,2,3,3-tetradeuteriobutanes are obtained. This suggests the metallocyclopentane is in equilibrium with a bis(ethylene) structure, wherein olefin rotation would give the observed label scrambling (23). The analogous metallocyclohexane, $Cp_2Ti(CH_2)_5$, decomposes primarily to pentane and pentene, but some methane, ethylene and butene are also detected; the yield of methane is substantially increased by added PR_3 or irradiation. Cleavage of an α-C-C bond to produce $Ti=CH_2$ was proposed, with the balance of hydrogens coming from the Cp rings. In support, both $(C_5D_5)_2Ti(CH_2)_5$ and $(C_5H_5)_2Ti(CD_2(CH_2)_3CD_2)$ give CH_2D_2 as the major isotopic form of methane (24). Metallocycles $Cp_2Ti(CH_2(SiMe_2)X(SiMe_2)CH_2)$ ($X=CH_2$, O, $SiMe_2$) and $Cp_2Ti(CH_2(SiMe_2)_2CH_2)$ have also been prepared (25).

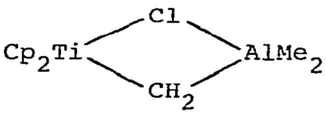
The decomposition of $MeTiCl_3$ in ether has been reexamined: at around 0^o, CH_4 is produced (plus traces of C_2H_6 and CH_3CHO); good second-order kinetics are followed over the first half of the reaction only. In ether-d_{10} about 5% each CH_2D_2 and CH_3D are formed at 0^o; more CH_3D is obtained at higher temperature. Apparently more than one pathway is operating (26). Kinetic studies on decomposition of a variety of Ti-alkyls show a "compensation effect"; rates increase with activation energy, indicating factors causing the latter to increase also cause an increase in the preexponential factor (27). Photodecomposition of Cp_2TiMe_2 gives 1.8 moles of CH_4/Ti; in the presence of styrene or methyl methacrylate, only 1 mol CH_4 is obtained, plus polymer. Labelling shows the polymer incorporates one Me from the complex per chain. $Cp_2Ti(CD_3)_2$ gives only CD_3H (a conflicting result was reported last year, but the wavelength of irradiation was different); it was proposed that the initial step gives CH_4 + $Cp(C_5H_4)TiMe$ with the latter acting as polymerization initiator (28).

Several groups have examined Cp_2TiPh_2. Thermal decomposition has been suggested to go via a benzyne-type intermediate; heating Cp_2Ti(m- or p-tolyl)$_2$ under CO_2, followed by methanolysis, gives a mixture of methyl m- and p-toluate. However, the relative amounts of products depend on which isomer was used, indicating that the benzyne route is not the only one operating (29). Photolysis of Cp_2TiPh_2 gives substantial amounts of biphenyl (in contrast to the thermal reaction) in addition to benzene (30,31). Intermediate ESR signals were observed, suggesting at least some homolysis (30); Cp_2Ti(tolyl)$_2$ in benzene gave a mixture of Ph-tolyl and bitolyl, with no loss of regiospecificity, excluding a benzyne intermediate. It was proposed that both homolysis and direct reductive elimination occur under irradiation (31). Photolysis of Cp_2TiPh_2 in the presence of PhCCPh gives metallocycle plus some stilbene, indicating Ti-H species can form (31); whereas the thermal reaction of Cp_2TiPh_2 with acetylenes gives titanaindenes:

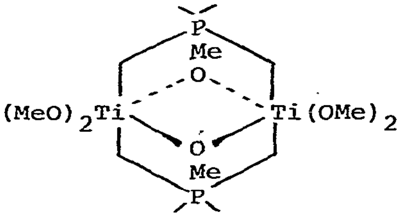


which probably form via a benzyne species. Crystal structures were determined for R=R'=C_6F_5 and for R=Ph, R'=$SiMe_3$ (32).

Novel titanium methylene complexes were obtained by the reaction of Cp_2TiCl_2 with $AlMe_3$, to form $Cp_2TiCH_2AlClMe_2$; $Cp_2TiCH_2AlMe_3$ was also prepared. NMR considerations suggest a doubly-bridged structure:



This compound effects homologation of olefins (e.g., ethylene is converted to propylene) and shows Wittig-type chemistry with organic carbonyl compounds; both types of behavior were previously observed for Ta alkylidenes. The homologation is thought to involve metallocyclobutane formation followed by a hydride shift; small amounts of cyclopropanes were detected in certain cases (33). Reaction of $TiCl(OMe)_3$ with Me_3PCH_2 gives $Ti_2(OMe)_6((CH_2)_2PMe_2)_2$; the crystal structure reveals this to be a bridged system with "clamps":



The Ti–Ti distance is 3.25 Å (34).

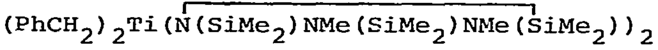
Several Ti-alkyls of oxidation state less than 4 are reported. $TiCl_4$ plus $LiCH(SiMe_3)_2$ gives TiR_3; in contrast, both Zr and Hf give MR_3Cl with this alkyl (35). $Ti(acac)_3$ with $(PhCH_2)_2Mg$ gives $Ti(PhCH_2)_3 \cdot nEt_2O$, stable only below 0° (36). Formation of TiR_3 from TiR_4 and EtLi, reported last year, is the subject of another paper (37). Cp_2TiR_2 (R = Ph, $PhCH_2$) forms an "ate" complex, $Cp_2TiR_4{}^{2-}$, with LiR at -78^o; at -20^o it decomposes to R_2Ti -- thermally stable black solids with low magnetic moments. Both are soluble and appear to be polymeric and dimeric respectively; this might explain the low magnetism, but adducts with dioxane, such as $Ti(CH_2Ph)_2(dioxane)_3$ have similarly low moments (0.5 B.M.) (38).

M(IV) alkyls reported include $Ti(cyclohexyl)_4$, stable at low temperature (39); $Zr(CH_2CMe_2Ph)_4$ (40); and $TiCl_n(CH_2SiR_3)_{4-n}$ (n = 1-3, various R); the latter are olefin polymerization catalysts (41). A flow-ESR study on the reaction of $TiCl_4$ with LiR suggests a single electron transfer mechanism:

$$\begin{aligned} RLi + TiCl_4 &\longrightarrow R\cdot + TiCl_4{}^- + Li^+ \\ TiCl_4{}^- &\longrightarrow TiCl_3 + Cl^- \\ R\cdot + TiCl_3 &\longrightarrow \text{products} \end{aligned}$$

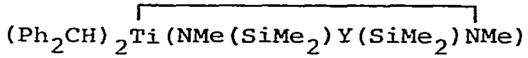
based on the appearance and disappearance of R• (42). The reaction of $TiCl_4$ with $AlEt_3$ as a function of reactant ratio has been studied (43).

$TiCl_2(OPh)_2$ reacts with $Mg(CH_2SiMe_3)_2$ to give $TiR_2(OPh)_2$; with $MgMe_2$, an unstable paramagnetic compound is formed, probably $[TiMe(OPh)_2]_n$ (11). $TiX(OR)_3$ (X = OR, Me or Cp) plus $AlMe_3$ gives (by NMR and cryoscopic molecular weight) $TiXMe(OR)_2 \cdot AlMe_2(OR)$ (44). Complexes with silylamide ligands,



$$(PhCH_2)_2Ti(N(SiMe_2)NMe(SiMe_2)NMe(SiMe_2))_2$$

and



$$(Ph_2CH)_2Ti(NMe(SiMe_2)Y(SiMe_2)NMe)$$

(Y = NMe, CH_2 or none) show substantial thermal stability; an x-ray structure for the first is reported (45).

Complexes with a bulky R group, $Cp_2ZrX(CH(SiMe_3)_2)$ (X = H, Cl, R') show high barriers to rotation about the Zr-C bond ($\Delta G^{\ddagger}$ = 10-15 kcal/mol). The hydride appears to be dimeric both in solution and in the vapor phase (from the mass spectrum). The crystal structure (X = Ph) shows relatively long Zr-C bonds and a large CZrC angle (46). The barrier to rotation about Zr-C was found to be at least 6 kcal/mol in Cp_2ZrMe_2 (from T_1 measurements) as well as in other transition metal methyls (47). No silyl complexes could be isolated from Cp_2TiCl_2 plus $LiSiMe_3$, but $Ti(SiMe_3)_4$ was obtained at low temperature (48). $(Cp_2TiCl)_2O$ + MeLi gives $(Cp_2TiMe)_2O$, notably thermally and air-stable (49).

Full papers appeared on the (C,N) chelates $Cp_2Ti(CH_2C_6H_4\text{-}\underline{o}\text{-}NMe_2)$, $Cp_2Ti(C_6H_4\text{-}\underline{o}\text{-}CH_2NMe_2)$ (50) and (dipivaloylmethanato)Ti(chelate)$_2$ (51). The crystal structure of $Cp_2Ti(C_6H_4\text{-}\underline{o}\text{-}NMe_2)$ has been determined (52). Complexes Cp_2TiR have been prepared where R = $(CH_2)_nXCH_3$, n = 3 or 4, X = O or S; these appear (by IR and failure to add N_2) to be chelated through X, with stability order n = 3 > 4; X = O > S. For n = 4, an interesting decomposition to Cp_2Ti(methallyl) and CH_3XH was observed (53). Cp_2TiMe (in situ from Cp_2TiCl and LiMe) reacts with aromatic amines such as pyridine to give Cp_2Ti(2-pyridyl), demonstrated by cleavage with DCl or I_2; the stability suggests coordination through N as well as C (54).

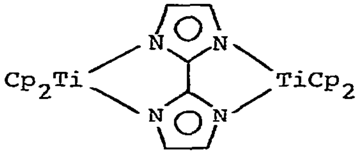
CYCLOPENTADIENYL COMPLEXES

An improved crystallographic structure determination on Cp_4Zr confirms that there are three η^5 and one η^1 rings, formally 20 electrons; the η^5-rings are not tilted but are further from Zr than usual (55).

Cp_2MX_2 complexes with chiral elements continue to attract interest. Menthyl Cp and neomenthyl Cp were used to make $Cp_2'MCl_2$ (M = Ti, Zr) and $CpCp'TiCl_2$; the crystal structure of Cp(menthyl Cp)$TiCl_2$ was determined (56). $(RCp)_2MCl_2$ and $(RCp)CpMCl_2$ (M = Zr, Hf), where RCp is derived from a fulvene, were prepared, the latter from $CpMCl_3$ for which preparative details are given (57). From these, (RCp)CpMClX (X = OR, CH_2Ph) were prepared and the chiral center at M investigated by NMR (58). Also studied were $(C_5H_4(CHMePh))_2TiCl(C_6F_5)$ and $(C_5H_4(CHMePh))CpTiCl(C_6F_5)$; enantiomers were resolved by replacing Cl by a chiral alkoxide, separating by chromatography, and removing the OR^* with HCl (59). $(C_5H_4(CH_2Ph))_2ZrCl_2$ is triboluminescent and piezoelectric; the crystal structure showed no unusual features which might account for this behavior (60).

Preparative details for Cp_2TiBH_4 have been reported (61). $CpTiCl_3$ plus $LiBH_4$ gives $CpTiCl(BH_4)$ and $CpTi(BH_4)_2$ (62). Reduction of Cp_2TiCl_2 by $LiAlH_4$ gives chloro and/or hydrido bridged fulvalenide complexes, $(C_{10}H_8)(CpTi)_2(\mu\text{-}X)(\mu\text{-}Y)$ where X, Y = H, Cl (63). A neutron diffraction study on $(MeCp)_2Hf(BH_4)_2$ shows that each BH_4 is bidentate but the two Hf–H distances are significantly different; the structure may be related to the facile bridge-terminal hydrogen exchange, which remains fast on the NMR time scale to -155^o (64).

Antiferromagnetic interactions in bridged $Cp_2Ti(III)$ systems continue to be investigated at Illinois. $(Cp_2Ti)_2(\mu\text{-pyrazolyl})_2$ was prepared and its structure determined; the Ti–Ti distance is 4.339 Å and the Ti_2N_4 ring lies in a chair conformation (65). The magnetic susceptibility shows no antiferromagnetic exchange, but weak exchange was inferred from the ESR spectrum. In contrast, $(Cp_2Ti)_2$(biimidazolyl), for which the Ti–Ti distance is much longer (6.02 Å), shows stronger coupling ($-J \sim 20\ cm^{-1}$) (66).



Di- and trinuclear Cp_2Ti complexes from uracil and cyanuric acid, respectively, also exhibit very weak coupling (67). The crystal structure of $Cp_2Ti(\mu\text{-}Cl)_2Mn(\mu\text{-}Cl)_2TiCp_2$ was determined; magnetic studies were compared to analogs with diamagnetic central metals Zn or Be (68).

^1H and ^{13}C NMR spectra were observed for $(Cp_2TiCl)_2$, $Cp_2TiCl(NCMe)$ and Cp_2TiBH_4; paramagnetic shifts are similar to those in previously studied Cp_2V (69). Dipole moments of Cp_2TiCl_2, $CpTiCl_3$, $(Cp_2TiCl)_2O$ and Cp_2TiCl were measured; the last is not zero (4.23 D in benzene) indicating that the symmetric solid-state structure is not entirely maintained in solution (70). Polarographic studies on Cp_2TiX_2 and $CpTiX_3$ were reported for X = Cl, OAr (Ar = aryl group); the results were interpreted by the following scheme (71):

$$Cp_2TiCl_2 \xrightarrow{e^-} Cp_2TiCl + Cl^- \xrightarrow{e^-} Cp_2Ti + Cl^- \xrightarrow{e^-} Cp_2Ti^{\overset{\bullet}{-}}$$

$$Cp_2TiCl(OAr) \xrightarrow{e^-} Cp_2Ti(OAr) + Cl^- \xrightarrow{e^-} Cp_2Ti(OAr)^{\overset{\bullet}{-}}$$

The cation $(Cp_2Ti(H_2O))_2O^{2+}$ has been prepared by two routes and its crystal structure determined with $S_2O_6^{2-}$ (72) and ClO_4^- (73) counterions; both show nearly linear Ti-O-Ti (177° and 176°, respectively). Cp_2MCl_2 (M = Ti, Zr, Hf) reacts with $LiCo_3(CO)_{10}$ to give $Cp_2MCl(OCCo_3(CO)_9)$ (the Ti example was previously made from $Co_2(CO)_8$; see 1976 survey) and $Cp_2M(OCCo_3(CO)_9)_2$; several crystal structures were determined and are quite similar to the earlier Ti structure (74). $CpTiCl_3$ + $NaCo(CO)_4$ gives $CpTi(OCCo_3(CO)_9)_2(Co(CO)_4)$: tetrahedral Ti with one Cp, two alkoxide, and one Co coordinated; Ti-Co = 2.614 Å (75). Reaction of $CpTiCl_3$ with $(H_3P)W_{11}O_{39}^{4-}$ gives $(CpTi)PW_{11}O_{39}^{4-}$, the first polyoxoanion-supported organometallic; spectral data (IR, ^1H and ^{17}O NMR) are consistent with a structure derived from known $PW_{12}O_{40}^{3-}$ by replacing WO^{4+} with $CpTi^{3+}$ (76).

Reactions of CpTi complexes with NO have been examined. $(Cp_2TiCl)_2$ plus NO gives $(Cp_2TiCl)_2O + N_2O$, while $Cp_2Ti(CO)_2$ gives CO_2, N_2 and an uncharacterized Ti product; Cp_2Ti plus N_2O gives a new compound, $(Cp_2Ti)_2O$, and N_2 (77). Cp_2TiCl_2 and NO yield N_2 and an uncharacterized Ti=O species. Several other reactions involving nitrogen species were examined as well: $CpTiCl_3$ reacts with PhN_2SiMe_3 to form $CpTiCl_2(N_2Ph)$ and with $Me_3SiN{=}PPh_3$ to give $CpTiCl_2(NPPh_3)$ (78). Cp_2TiCl_2 plus $Me_3SiN_2SiMe_3$ gives $Cp_2TiNN(SiMe_3)_2$, analogous to the vanadium product previously reported (79). Cp_2TiCl forms an adduct with a nitroxide radical, $Cp_2TiCl(ONR_2)$ (80).

Complexes Cp_2TiX_2 (X = NO_2, ONO, ONO_2) (81) and $Cp_2TiX(CN)$ (X = Br, I) (82) have been prepared, the latter from $Cp_2Ti(CO)_2$ + XCN. $Cp_2Ti(IV)$ complexes with salicylidenimine (83) and oxime (84,85) ligands have also been reported. The variable temperature NMR of Cp_2TiS_5 shows a barrier of 18.2 kcal/mol to inversion of the chair conformation of the TiS_5 ring (86). Complexes $(Cp_2Ti(XPh))_2$ (X = S, Se) (87) and a variety of CpTi (88,89) and CpZr (90,91) dithiocarbamate complexes were prepared. The crystal structure of $CpTi(S_2CNMe_2)_3$ is quite similar to the previously reported Zr analog (92). The alkylxanthate complexes $CpZr(S_2COR)_3$ (R = Me, Et) have the same basic structure according to spectroscopic evidence

(93). Reaction of $CpZrX(acac)_2$ with bromine gives bromination of both acac methine carbons without affecting the Cp ring (94).

OTHER π-BONDED COMPLEXES

The crystal structure of $Cp_2Ti(CO)(PhCCPh)$, the only simple η^2-olefin or acetylene complex of this group, has been reported; it shows no particular difference from other acetylene complexes. In solution it decomposes to give $Cp_2Ti(CO)_2$ and $Cp_2Ti(CPh)_4$ (95).

The apparatus used to make $Ti(C_6H_6)_2$ by metal vapor methods has been described in a patent (96). Condensation of potassium vapor into a solution of $TiCl_4$ and arene in THF at -100^o leads to $Ti(toluene)_2$ and $Ti(mesitylene)_2$ (97). Treatment of $TiCl_4$ with $AlClEt_2$ and C_6Me_6 gives $(C_6Me_6)TiCl_2{}^+AlCl_4{}^-$, which reacts with water to give previously known $(C_6Me_6)_3Ti_3Cl_6{}^{3+}$ (98).

An SCF-MO calculation for $CpM(C_7H_7)$ (M = Ti, V, Cr) indicates that in Ti the C_7 ring is most tightly bound and has the highest negative charge (99). $Ti_2(C_8H_8)_3$ has been made by the metal vapor method; it is reduced by K to $Ti_2(C_8H_8)_3{}^{2-}$ which, surprisingly, shows only one NMR peak; accidental degeneracy was suggested (100).

APPLICATIONS IN SYNTHESIS AND CATALYSIS

Hydrozirconation is now beginning to be used in complex syntheses: addition of Cp_2ZrHCl followed by iodination gave stereospecific conversion of an alkyne to an iodoolefin, a key intermediate in the total synthesis of the erythromycin precursor erythronolide B (101). Cp_2ZrHCl adds to $HC{\equiv}C\text{-}CH(OSiMe_3)C_5H_{11}$; the resulting alkenyl Zr undergoes conjugate addition to a cyclopentenone in the presence of a Ni catalyst to give a useful intermediate in prostaglandin synthesis (102). Hydrozirconation was used to monohydrogenate vitamin D_3 (a conjugated triene) in improved yields over previous methods (103).

Alkenyl Zr complexes formed by hydrozirconation of terminal acetylenes couple with alkenyl halides in the presence of Pd(O) to give dienes with good yield and stereospecificity (104). $Cp_2TiClMe$ adds to PhCCPh, giving methyl stilbene after hydrolysis; dialkylacetylenes give allenes, probably by β-hydride elimination from the intermediate alkenyl complex (105). Terminal acetylenes react readily with Cp_2ZrCl_2 plus Me_3Al to give $RMeC{=}CHAlMe_2$; Zr can be used catalytically (106,107). Coupling with alkyl halides to give trisubstituted olefins is best achieved by Pd(O) with $ZnCl_2$ as co-catalyst (108). Cp_2TiCl_2 catalyzes hydromagnesiation of alkenols, leading to lactones (109); additional work on Ti-promoted alkylation of alkenols has appeared (110,111).

A number of examples of the use of Ti to catalyze addition of aluminum hydrides to olefins have been reported (112-118); also MgH_2 can be used (119). $Cp_2ZrCl(BH_4)$ reduces aldehydes and ketones to alcohols; selectivity and reactivity are comparable to $NaBH_4$ (120). Low-valent species obtained by reduction of Ti or Zr compounds have been used for deoxygenation of epoxides (121,122) and alcohols (123-124), reductive coupling of carbonyl compounds (125-128), and hydrogenolysis of alkyl halides (129,130); in none of these has the involvement of organometallic intermediates been strongly implicated. An ion cyclotron resonance study on the reaction of $TiCl_4$ with carbonyl compounds suggests organotitanium intermediates in some cases (131). The combination $TiCl_4$ + Zn + CH_2Br_2 effects methylenation of carbonyls (Wittig reaction) (132); again it is not known if organotitanium is involved, but the report of a stable Ti methylene which reacts similarly (vide supra) is most suggestive.

Japanese language reviews of hydrozirconation (133) and the use of Ti in synthesis (134) have appeared.

Compounds $Cp_2'MMe_2$ and $Cp_2'MH_2$ (M = Zr, Hf) are catalysts for olefin hydrogenation at 80°. Optically active $Cp(C_5H_4(CHMePh))ZrMe_2$ was prepared but gave no optical induction in hydrogenation of prochiral alkenes (135).

$Cp_3(C_5H_4)Ti_2$ catalyzes polymerization of acetylene; mostly trans was obtained at room temperature, cis at -80° (136). An ESR study was carried out on the olefin polymerization catalyst formed from $Ti(CH_2Ph)_4$ and silica (137). A review on industrial applications of homogeneous catalysis (very interesting and useful, especially to academic chemists) includes a brief section on Ti-catalyzed olefin polymerization (138).

REFERENCES

1 G. Fachinetti, C. Floriani, A. Roselli and S. Pucci, J. Chem. Soc., Chem. Commun., (1978)269.

2 J. M. Manriquez, D. R. McAlister, R. D. Sanner and J. E. Bercaw, J. Am. Chem. Soc., 100(1978)2716.

3 B. Demerseman, G. Bouquet and M. Bigorgne, J. Organomet. Chem., 145(1978)41.

4 G. Fachinetti, C. Biran, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Am. Chem. Soc., 100(1978)1922.

5 G. Fachinetti, C. Biran, C. Floriani, A. Chiesi-Villa and C. Gustini, Inorg. Chem., 17(1978)2995.

6 J. Chatt, J. R. Dilworth and R. L. Richards, Chem. Rev., 78(1978)589.

7 P. Sobota and B. Jezowska-Trzebiatowska, Coord. Chem. Rev. 26(1978)77.

8 J. E. Bercaw, in "Recent Developments in Nitrogen Fixation" (W. E. Newton, J. R. Postgate and C. Rodriguez-Barreco, Eds.), Academic Press, London, 1977, pp. 25-39.

9 J. M. Manriquez, D. R. McAlister, E. Rosenberg, A. M. Shiller, K. C. Williamson, S. I. Chan and J. E. Bercaw, J. Am. Chem. Soc., 100(1978)3078.
10 M. J. S. Gynane, J. Jeffrey and M. F. Lappert, J. Chem. Soc., Chem. Commun., (1978)34.
11 A. Flamini, D. J. Cole-Hamilton and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1978)454.
12 V. B. Shur, E. G. Berkovich, S. M. Yunusov, Sh. M. Mamedov, I. L. Nizker and M. E. Volpin, Izv. Akad. Nauk SSSR, Ser. Khim., (1978)2630.
13 J. N. Armor, Inorg. Chem., 17(1978)203.
14 J. N. Armor, Inorg. Chem., 17(1978)213.
15 K. I. Gell and J. Schwartz, J. Am. Chem. Soc., 100(1978)3246.
16 D. R. McAlister, D. K. Erwin and J. E. Bercaw, J. Am. Chem. Soc., 100(1978)5966.
17 M. Yoshifuji, K. I. Gell and J. Schwartz, J. Organomet. Chem., 153(1978)C15.
18 K. I. Gell and J. Schwartz, J. Organomet. Chem., 162(1978)C11.
19 G. Erker and F. Rosenfeldt, Angew. Chem., 90(1978)640.
20 E. J. M. de Boer and J. H. Teuben, J. Organomet. Chem., 153(1978)53.
21 K.-H. Thiele and M. Panse, Z. Anorg. Allg. Chem., 441(1978)23.
22 P. Renaut, G. Tainturier and B. Gautheron, J. Organomet. Chem., 150(1978)C9.
23 R. H. Grubbs and A. Miyashita, J. Am. Chem. Soc., 100(1978)1300.
24 R. H. Grubbs and A. Miyashita, J. Am. Chem. Soc., 100(1978)7418.
25 H. Sakurai and H. Umino, J. Organomet. Chem., 142(1977)C49.
26 D. Dong, S. C. V. Stevens, J. D. McCowan and M. C. Baird, Inorg. Chim. Acta, 29(1978)L225.
27 P. E. Matkovskii, L. I. Chernaya, F. S. Dyachkovskii and N. E. Khrushch, Zh. Obshch. Khim., 47(1977)1841.
28 C. H. Banford, R. J. Puddephatt and D. M. Slater, J. Organomet. Chem., 159(1978)C31.
29 M. Kh. Grigoryan, I. S. Kolomnikov, E. G. Berkovich, T. V. Lysyak, V. B. Shur and M. E. Volpin, Izv. Akad. Nauk SSSR, Ser. Khim., (1978)1177.
30 M. Peng and C. H. Brubaker, Inorg. Chim. Acta, 26(1978)231.
31 M. D. Rausch, W. H. Boon and E. A. Mintz, J. Organomet. Chem., 160(1978)81.
32 J. Mattia, M. B. Humphrey, R. D. Rogers, J. L. Atwood and M. D. Rausch, Inorg. Chem., 17(1978)3257.
33 F. N. Tebbe, G. W. Parshall and G. S. Reddy, J. Am. Chem. Soc., 100(1978)3611.
34 W. Scharf, D. Neugebauer, U. Schubert and H. Schmidbaur, Angew. Chem., 90(1978)628.
35 G. K. Barker, M. F. Lappert and J. A. K. Howard, J. Chem. Soc., Dalton Trans., (1978)734.
36 K. Jacob, K.-H. Thiele and V. Dimitrov, Z. Anorg. Allg. Chem., 447(1978)136.
37 S. I. Beilin, S. B. Golshtein, B. A. Dolgoplosk, A. M. Krapivin, E. I. Tinyakova, I. Sh. Guzman and G. N. Bondarenko, Dokl. Akad. Nauk SSSR, 235(1777)99.
38 K.-H. Thiele, A. Röder and W. Mörke, Z. Anorg. Allg. Chem., 441(1978)13.
39 J.-B. Weber, J. Porret and A. Jacot-Guillarmod, Helv. Chim. Acta, 61(1978)2949.
40 W. G. Peet, F. N. Tebbe and G. W. Parshall, Res. Discl., 168(1978)21; Chem. Abstr., 89(1978)24489.
41 G. Sonner, K. G. Baumgarten, H. Reinheckel, S. Schroeder and K.-H. Thiele, E. Ger. Patent 128, 638; Chem. Abstr., 89(1978)109944.
42 G. A. Russell and D. W. Lawson, J. Organomet. Chem., 156(1978)17.

43 C. G. Kim, C. S. Pak and B. S. Choe, Hwahak Kwa Hwahak Kongop, 20(1977)208; Chem. Abstr., 88(1978)89744.
44 C. Blandy, M. T. Sadani and D. Gervais, Synth. React. Inorg. Metal-Org. Chem., 8(1978)381.
45 D. J. Brauer, H. Bürger and K. Wiegel, J. Organomet. Chem., 150(1978)215.
46 J. Jeffery, M. F. Lappert, N. T. Luong-Thi, J. L. Atwood and W. E. Hunter, J. Chem. Soc., Chem. Commun., (1978)1081.
47 R. F. Jordan, E. Tsang and J. R. Norton, J. Organomet. Chem., 149(1978)C53.
48 G. A. Razuvaev, V. N. Latyaeva, L. I. Vyshinskaya, A. V. Malysheva and G. A. Vasileva, Dokl. Akad. Nauk SSSR, 237(1977)605.
49 H. Surer, S. Claude and A. Jacot-Guillarmod, Helv. Chim. Acta, 61(1978)2956.
50 L. E. Manzer, J. Am. Chem. Soc., 100(1978)8069.
51 L. E. Manzer, Inorg. Chem., 17(1978)1552.
52 W. F. J. van der Wal and H. R. van der Wal, J. Organomet. Chem., 153(1978)335.
53 G. W. M. Visser and J. H. Teuben, J. Organomet. Chem., 144(1978)81.
54 B. Klei and J. J. Teuben, J. Chem. Soc., Chem. Commun., (1978)659.
55 R. D. Rogers, R. V. Bynum and J. L. Atwood, J. Am. Chem. Soc., 100(1978)5238.
56 E. Cesarotti, H. B. Kagan, R. Goddard and C. Krüger, J. Organomet. Chem., 162(1978)297.
57 P. Renaut, G. Tainturier and B. Gautheron, J. Organomet. Chem., 148(1978)35.
58 P. Renaut, G. Tainturier and B. Gautheron, J. Organomet. Chem., 148(1978)43.
59 J. Leblanc, C. Moise and J. Tirouflet, J. Organomet. Chem., 148(1978)171.
60 Y. Dusausoy, J. Protas, P. Renaut, B. Gautheron and G. Tainturier, J. Organomet. Chem., 157(1978)167.
61 C. R. Lucas, Inorg. Syntheses, 17(1977)91.
62 G. L. Soloveichik, B. M. Bulychev and K. N. Semeneko, Koord. Khim., 4(1978)1216; Chem. Abstr., 89(1978)163706.
63 H. Antropiusova, V. Hanus and K. Mach, Transition Met. Chem., 3(1978)121.
64 P. L. Johnson, S. A. Cohen, T. J. Marks and J. M. Williams, J. Am. Chem. Soc., 100(1978)2709.
65 B. F. Fieselmann and G. D. Stucky, Inorg. Chem., 17(1978)2074.
66 B. F. Fieselmann, D. N. Hendrickson and G. D. Stucky, Inorg. Chem., 17(1978)2078.
67 B. F. Fieselmann, D. N. Hendrickson and G. D. Stucky, Inorg. Chem., 17(1978)1841.
68 D. Sekutowski, R. Jungst and G. D. Stucky, Inorg. Chem., 17(1978)1848.
69 F. H. Köhler and D. Cozak, Z. Naturforsch., 33b(1978)1274.
70 N. A. Yakovleva, G. L. Soloveichik and B. M. Buylchev, Izv. Akad. Nauk SSSR, Ser. Khim., (1978)1409.
71 E. Laviron, J. Besançon and F. Huq, J. Organomet. Chem., 159(1978)279.
72 U. Thewalt and G. Schleussner, Angew. Chem., 90(1978)559.
73 U. Thewalt and B. Kebbel, J. Organomet. Chem., 150(1978)59.
74 B. Stutte, V. Bätzel, R. Boese and G. Schmid, Chem. Ber., 111(1978)1603.
75 G. Schmid, B. Stutte and R. Boese, Chem. Ber., 111(1978)1239.
76 R. K. C. Ho and W. G. Klemperer, J. Am. Chem. Soc., 100(1978)6774.
77 F. Bottomley and H. H. Brintzinger, J. Chem. Soc., Chem. Commun., (1978)234.

78 J. R. Dilworth, H. J. de Liefde Meijer and J. H. Teuben, J. Organomet. Chem., 159(1978)47.
79 N. Wiberg, H.-W. Häring, G. Huttner and P. Friedrich, Chem. Ber., 111(1978)2708.
80 V. A. Golubev, G. N. Voronina, L. I. Chernova, F. S. Dyachkovskii and P. E. Matkovskii, Zh. Obshch, Khim., 47(1977)1825.
81 R. S. Arora, M. S. Bhalla and R. K. Multani, Indian J. Chem., 16A(1978)169; Chem. Abstr., 88(1978)191015.
82 M. Morán and V. Fernandez, J. Organomet. Chem., 153(1978)C4.
83 R. Sharan, G. Gupta and R. N. Kapoor, Transition Met. Chem., 3(1978)282.
84 G. Gupta, R. Sharan and R. N. Kapoor, Transition Met. Chem., 3(1978)211.
85 R. Sharan, G. Gupta and R. N. Kapoor, J. Less-Common Met., 60(1978)171; Chem. Abstr., 90 (1978)23205.
86 E. W. Abel, M. Booth and K. G. Orrell, J. Organomet. Chem., 160(1978)75.
87 A. A. Pasynskii, I. L. Eremenko, Yu. V. Skripkin and V. T. Kalinnikov, Koord. Khim., 3(1977)1511; Chem. Abstr., 88(1978)23091.
88 N. K. Kaushik, B. Bhushan and G. R. Chatwal, Transition Met. Chem., 3(1978)215.
89 N. K. Kaushik, B. Bhushan and G. R. Chatwal, Synth. React. Inorg. Metal-Org. Chem., 8(1978)467.
90 V. K. Jain, V. Kumar and B. S. Garg, Inorg. Chim. Acta, 26(1978)197.
91 V. K. Jain and B. S. Garg, J. Inorg. Nucl. Chem., 40(1978)239.
92 W. L. Steffen, H. K. Chun and R. C. Fay, Inorg. Chem., 17(1978)3498.
93 V. K. Jain, R. K. Sharma and B. S. Garg, Inorg. Chim. Acta, 26(1978)51.
94 E. M. Brainina and L. I. Strunkina, Izv. Akad. Nauk SSSR, Ser. Khim., (1977)2599.
95 G. Fachinetti, C. Floriani, F. Marchetti and M. Mellini, J. Chem. Soc., Dalton Trans., (1978)1398.
96 M. L. H. Green, Brit. Patent 1,483,459; Chem. Abstr., 88(1978)74462.
97 P. N. Hawker, E. P. Kündig and P. L. Timms, J. Chem. Soc., Chem. Commun., (1978)730.
98 S. Dziergowski, R. Giezynski, M. Jarosz and S. Pasynkiewicz, J. Organomet. Chem., 152(1978)281.
99 J. D. Zeinstra and W. C. Nieuwpoort, Inorg. Chim. Acta, 30(1978)103.
100 S. P. Kolesnikov, J. E. Dobson and P. S. Skell, J. Am. Chem. Soc., 100(1978)999.
101 E. J. Corey, E. J. Trybulski, L. S. Melvin, K. C. Nicolaou, J. A. Secrist, R. Lett, P. W. Sheldrake, J. R. Falck, D. J. Brunelle, M. F. Haslanger, S. Kim and S.-E. Yoo, J. Am. Chem. Soc., 100(1978)4618.
102 M. J. Loots and J. Schwartz, Tet. Lett., (1978)4381.
103 A. W. Messing, F. P. Ross, A. W. Norman and W. H. Okamura, Tet. Lett., (1978)3635.
104 N. Okukado, D. E. van Horn, W. L. Klima and E. Negishi, Tet. Lett., (1978)3635.
105 D. E. van Horn, L. F. Valente, M. J. Idacavage and E. Negishi, J. Organomet. Chem., 156(1978)C20.
106 N. Okukado and E. Negishi, Tet. Lett., (1978)2357.
107 D. E. van Horn and E. Negishi, J. Am. Chem. Soc., 100(1978)2252.
108 E. Negishi, N. Okukado, A. O. King, D. E. van Horn and B. I. Spiegel, J. Am. Chem. Soc., 100(1978)2254.
109 J. J. Eisch and J. E. Galle, J. Organomet. Chem., 160(1978)C8.

110 H. E. Tweedy, P. E. Hahn, L. C. Smedley, A. V. Youngblood, R. A. Coleman and D. W. Thompson, J. Mol. Catal., 3(1978)239.
111 A. V. Youngblood, S. A. Nichols, R. A. Coleman and D. W. Thompson, J. Organomet. Chem., 146(1978)221.
112 F. Sato, S. Sato, H. Kodama and M. Sato, J. Organomet. Chem., 142(1977)71.
113 F. Sato, H. Kodama and M. Sato, Chem. Lett., (1978)789.
114 F. Sato, K. Oguro and M. Sato, Chem. Lett., (1978)805.
115 F. Sato, Y. Mori and M. Sato, Chem. Lett., (1978)833.
116 F. Sato, S. Haga and M. Sato, Chem. Lett., (1978)999.
117 K. Isagawa, M. Ohige, K. Tatsumi and Y. Otsuji, Chem. Lett., (1978)1155.
118 J. Tsuji, T. Yamakawa and T. Mandai, Tet. Lett., (1978)565.
119 E. C. Ashby and T. Smith, J. Chem. Soc., Chem. Commun., (1978)30.
120 T. N. Sorell, Tet. Lett., (1978)4985.
121 M. Berry, S. G. Davies and M. L. H. Green, J. Chem. Soc., Chem. Commun., (1978)99.
122 J. E. McMurry, M. G. Silvestri, M. P. Fleming, T. Hoz and M. W. Grayston, J. Org. Chem., 43(1978)3249.
123 S. C. Welch and M. E. Walters, J. Org. Chem., 43(1978)4797.
124 H. Ishikawa and T. Mukaiyama, Bull. Chem. Soc. Japan, 51(1978)2059.
125 J. E. McMurry, M. P. Fleming, K. L. Kees and L. R. Krepski, J. Org. Chem., 43(1978)3255.
126 P. Sobota, C. Wawrezenczyk and J. Otko, Bull. Acad. Pol. Sci. Chim., 25(1977)957; Chem. Abstr., 88(1978)145410.
127 J. Besançon and J. Tirouflet, C. R. Acad. Sci., Ser. C, 287(1978)113.
128 A. Kasahara and T. Izumi, Chem. Lett., (1978)21.
129 J. J. Brunet, R. Vanderesse and P. Caubere, J. Organomet. Chem., 157(1978)125.
130 O. Christofis, J. J. Habeeb, R. S. Steevensz and D. G. Tuck, Can. J. Chem., 56(1978)2269.
131 J. Allison and D. P. Ridge, J. Am. Chem. Soc., 100(1978)163.
132 K. Takai, Y. Hotta, K. Oshima and H. Nozaki, Tet. Lett., (1978)2417.
133 M. Yoshifuji, Yuki Gosei Kagaku Kyokaishi, 35(1977)675; Chem. Abstr., 88(1978)23000.
134 S. Kobayashi and T. Mukaiyama, Kagaku No Ryoiki Zokan, 117(1977)191; Chem. Abstr., 89(1978)98919.
135 S. Couturier and B. Gautheron, J. Organomet. Chem., 157(1978)C61.
136 S. L. Hsu, A. J. Signorelli, G. P. Pez and R. H. Baughman, J. Chem. Phys., 69(1978)106.
137 N. G. Maksimov, G. A. Nesterov, V. A. Zakharov, P. V. Stchastnev, V. F. Anufrienko and Yu. I. Yermakov, J. Mol. Catal., 4(1978)167.
138 G. W. Parshall, J. Mol. Catal., 4(1978)243.