σ-Alkyl and -Aryl Complexes of the Group 4–7 Transition Metals

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I. Introduction

Transition metal complexes containing alkyl or aryl ligands have proliferated in the past decade. One of the most striking developments is the synthesis of "binary" complexes containing only σ-alkyl or -aryl ligands which violate previously accepted stability rules, such as the principle that stable metal alkyls must be diamagnetic or that they must be coordinatively saturated (the 18 electron rule).[1]

We intend to summarize recent advances in transition metal alkyl and aryl chemistry and will emphasize the early transition metals (groups 4–7) since the most exciting fundamental developments involve these elements. Generally group 8 metal alkyl chemistry is still well represented by earlier comprehensive reviews.[2,3] More recent discussions of the metal–carbon bond are also available[4–7] (see also section VI), while other sources cover earlier or more specialized material.[8–16]

II. Binary Alkyl Complexes[†]

Transition metal compounds bearing only σ-alkyl ligands have previously been so scarce and so little studied that the impression arose that binary metal alkyls are inherently unstable. The key to dispelling this fallacy came with the understanding that transition metal alkyls can decompose via β-hydrogen "elimination" (or "abstraction"), which is not common among main group alkyls under similar mild experimental conditions. Subsequently people recognized that alkyls which have no β-hydrogen should form stable complexes. (Stability normally refers to thermal stability, a property which has not yet been measured in a standard way.) Several research groups reported examples almost simultaneously. Particularly striking are WMe_6 and $Ti(CH_2SiMe_3)_4$, which grossly violate the 18 electron stability rule, and paramagnetic $V(CH_2Ph)_4$.

Others prepared stable compounds containing *tert*-butyl or norbornyl groups. In the former the β hydrogen appears to be sterically inaccessible to the metal atom. In the latter β-elimination is unfavorable because unsaturation at a bridgehead carbon would result (Bredt's rule).

Though suppression of *intra*molecular decomposition (primarily β-elimination) has received the greatest emphasis, the fact that binary complexes with large alkyl ligands lacking a β hydrogen are prepared more easily and are more stable than the corresponding methyl complexes almost certainly can be attributed also in part to the concomitant suppression of *inter*molecular decomposition reactions. The interesting consequence in some instances is that *intramolecular α-hydrogen abstraction* becomes a favored decomposition mode.

[†] For brevity, "alkyl" will usually be a general term including aryl and alkaryl, and ligands containing Si in the β position such as $-CH_2SiMe_3$.

Quite generally, the new binary metal alkyls react with air and moisture and are only modestly stable thermally. The usual synthesis involves reaction of a Grignard or organolithium reagent with a transition metal halide as in

$$4PhCH_2MgCl + ZrCl_4 \xrightarrow{Et_2O} Zr(CH_2Ph)_4$$

Exact experimental details are often critical. We classify binary alkyls by ligand type and discuss their preparation and chemistry below.

A. Neutral

1. Methyl

In general, binary methyl complexes are extraordinarily stable *relative to* those containing alkyls bearing a β hydrogen. Complexes are known for Ti, Zr, Ta, Nb, Cr, W, and Mn.

Clauss and Beermann[17] first prepared bright yellow $TiMe_4$ in 1959 from methyllithium or a methyl Grignard reagent and $TiCl_4$ in diethyl ether at −78°. Inverse addition ($TiCl_4$ to the alkylating agent) was later found to give a smoother reaction.[18] Tetramethyltitanium and ether codistill from the reaction mixture at ca. −30°. In ether it decomposes near room temperature to give methane, traces of ethylene and ethane, and a black residue containing carbon, hydrogen, and Ti.[19,20] Crystalline $TiMe_4$, obtained by removing ether in vacuo from a hexane-ether solution at −78° (ref 18), begins to decompose a few degrees above −78°.

Tetramethylzirconium is prepared in ether-toluene at −45° from methyllithium and $ZrCl_4$. Codistillation gives a red-brown ether solution of $ZrMe_4$ which evolves 4.0 mol methane per zirconium on hydrolysis.[21] No further characterization or reactions have been reported.

Methyllithium (2 mol) reacts with $TaMe_3Cl_2$ at −78 to 0° in ether to give $TaMe_5$ which can be isolated as volatile, pale yellow needles which melt at ca. 10° to a yellow oil.[22] It decomposes smoothly at 25° in several hours to give methane (ca. 3.2 mol) as the only detectable gaseous product. Its ^1H NMR spectrum in toluene-d_8 at −10° shows a single sharp singlet at τ 9.18 and its mass spectrum a peak corresponding to $TaMe_4^+$. Like $TiMe_4$, its solutions in ether appear somewhat more stable than the pure complex; it may be stabilized by coordination of ether. The analogous reaction of $NbMe_2Cl_3$ with 3 mol of LiMe gives a yellow-orange ether solution of a product which decomposes smoothly between −20 and −10°. Though a stable, seven-coordinate adduct, $NbMe_5L_2$ (L_2 = e.g., a chelating phosphine), was isolated after adding L_2 to the ether solution, firm conclusions concerning the existence of $NbMe_5$ must await further studies.

Hexamethyltungsten can be prepared in ca. 40% yield from WCl_6 and *3* mol of LiMe in ether at −20° (ref 23, 24). The yield is reportedly extremely sensitive to this reactant ratio, and evidence suggests WMe_6 does not form directly. Traces of oxygen may also be required.[25] It has also been prepared from WCl_6 and $AlMe_3$ in aliphatic hydrocarbons.[25] WMe_6 can be extracted into pentane or sublimed onto a −10° probe and melts and decomposes near room temperature to give ca. 3 mol of methane containing <5% ethane. In toluene-d_8 it gives a single ^1H NMR resonance at τ 8.38. The WMe_5^+ peak was the highest found in its mass spectrum. It can be characterized further by reaction with O_2, R_2NH, and halogens (X_2) to give $W(OMe)_6$, $W(NR_2)_6$, and WX_6, respectively, and with NO to give $WMe_4\{ON(Me)N{=}O\}_2$ (see section VII.G). A photoelectron spectrum is consistent with octahedral W(VI) bound to six carbon ligands.[26]

Isolation of WMe_6 and $TaMe_5$ suggests that other third-row binary methyl complexes, $HfMe_4$ and $ReMe_7$, should be isolable though a direct method of preparing the latter is not obvious. $ReMe_6$ has recently been mentioned briefly.[25]

Only binary methyl complexes with the metal in its highest common formal oxidation state (Ti^{IV}, Ta^{V}, W^{VI}) are well characterized. A few lower valent complexes have been reported, but only dimethylmanganese has been isolated. Reaction of $TiCl_3(THF)_3$ with LiMe in ether[17] or MeMgCl in THF or ether[27] gives a dark-green solution believed to contain trimethyltitanium. Brown-red $CrMe_3$ and black $CrMe_2$ have been postulated in analogous reaction schemes,[17] while $CrMe_4$ is probably formed from $Cr(OCMe_3)_4$ and 4LiMe in pentane at −78° (ref 28, 29). All are exceedingly unstable and no adducts have been isolated. It was noted[29] that codistillation of $CrMe_4$ and petroleum in vacuo gave a considerably less stable solution (it decomposed slowly at −60°) than when lithium reagent was present. Dimethylmanganese (from MnI_2 and 2LiMe in ether[30,31]), unlike the complexes discussed so far, is insoluble in ether and assumed to be polymeric. It has also been prepared in THF,[32] coordination of which apparently prevents polymerization.

Binary methyl complexes have low formal valence electron counts (e.g., 8 for $TiMe_4$) and consequently readily form adducts with donor ligands when sterically possible. Adducts of tetramethyltitanium have been studied to the greatest extent.[33-35] Both five-coordinate ($TiMe_4L$) and six-coordinate complexes ($TiMe_4L_2$) have been isolated. Those which can be characterized are monomeric in aromatic solvents. In general, $TiMe_4L$ complexes are less stable. A qualitative thermal stability series is L = diox < NMe_3 < PMe_3 < py. For $TiMe_4L_2$ it is L_2 = TMEDA < $2PMe_3$ < phen < bpy < dmpe. For example, $TiMe_4$(diox) explodes at 0° while $TiMe_4$(dmpe) sublimes in vacuo at 30–40° without decomposition. Greatest stability occurs when two coordination sites are strongly occupied, the implication being that vacant metal coordination sites allow at least initiation of decomposition. This phenomenon has been observed somewhat more directly for remarkably stable $TaMe_5$(dmpe) and $NbMe_5$(dmpe).[22] The ^1H NMR spectrum of $TaMe_5$(dmpe) at 105° exhibits a triplet resonance for five methyl groups coupled to two phosphorus nuclei. At slightly higher temperatures the triplet becomes a singlet, coordinated dmpe exchanges with added dmpe, and the complex rapidly decomposes. Weak 1:1 adducts of WMe_6 with PPh_2Me, $PPhMe_2$, and PPh_2Et are isolable at low temperature, but the ligands dissociate readily in solution at room temperature.[24] Finally, apparently even weak solvent adducts are more stable than the parent compound judging by enhanced stability in solvents such as diethyl ether.

2. Phenyl

Contrary to popular belief, phenyl complexes are not inherently more stable than alkyl complexes, unless the alkyl contains a β hydrogen. Neutral binary phenyl complexes are scarce and difficult to prepare. Metal reduction and biphenyl formation are common. A low energy decomposition route involving ortho hydrogen abstraction, strictly analogous to β-hydrogen abstraction, may be responsible for these difficulties (see section VI.A).

The MPh_4 complexes where M = Ti,[36] Zr,[37] or V[38] have been prepared at low temperature in ether and characterized by reaction with $HgCl_2$ to give PhHgCl. All decompose readily at 0°:

$$MPh_4 \rightarrow MPh_2 + \text{biphenyl } (M = Ti, V)$$

$$ZrPh_4 \rightarrow [ZrPh_2(\text{ether})]_2 + 0.5\text{biphenyl} + C_6H_6$$

No details of the latter, which apparently requires a source of H, were proposed. Black, crystalline $[ZrPh_2(\text{ether})]_2$ can be isolated in 95% yield and has been characterized well. It is very soluble in ether, THF, dioxane, and aromatic hydrocarbons and poorly soluble in saturated hydrocarbons. It decomposes at high temperatures according to the stoichiometry

$$[\mathrm{ZrPh_2(ether)}]_2 \xrightarrow{50-180°} 2\mathrm{Zr(Ph)(OEt)} + \mathrm{C_6H_6} + 0.5\mathrm{C_6H_5{-}C_6H_5} + 0.5\mathrm{C_2H_6} + 1.5\mathrm{C_2H_4}.$$

The exact nature of black, pyrophoric $TiPh_2$ and VPh_2 has not been fully elucidated.

Reduction can be minimized by appropriate choice of reactants, order of addition, rate of addition, and temperature. For example, good yields of $TiPh_4$ are obtained by reaction of $TiCl_4L_2$ (L = py, pip, or quin) and PhMgBr in ether at −16° (ref 39). The authors attribute this favorable result to precipitation of $MgBr_2L_x$ during the reaction. They also suggest that the crystalline "$TiPh_4$" which was isolated at −80° in ether[36] was actually sparingly soluble $TiPh_4 \cdot nMgX_2$ (X = halide). Further studies showed that substitution of $Ti(OCMe_3)_4$ for $TiCl_4$ and use of inverse addition gives $Ti(OCMe_3)_4 \cdot n$PhMgBr which disproportionates on addition of dioxane to give $TiPh_4$, $Mg(OCMe_3)_2$, and sparingly soluble $MgBr_2(diox)_2$. The best system appears to be that employing $Ti(OCMe_3)_4$ and $MgPh_2$ which gives a smooth reaction to form $TiPh_4$ with essentially no reduction of Ti^{IV} (ref 40). These authors conclude that, at least in the case of titanium, magnesium halides and other Lewis acids contribute to instabilities of reaction mixtures containing TiR_4. Accordingly, in contrast to previous reports,[36,41] they found pure $TiPh_4$ does not decompose in refluxing ether.[42] In the crystalline state, however, $TiPh_4$ turns black in a few minutes at room temperature. It is monomeric in benzene.

A few adducts of $TiPh_4$ were prepared for spectroscopic purposes.[35] Apparently only orange $TiPh_4(bpy)$, stable at 0°C, was isolated, though they observed adducts with TMPDA, py, TMEDA, and TMMDA in solution.

The major class of binary phenyl complexes are those of chromium. The early work of Hein was shown by Zeiss and Tsutsui in 1954 to involve η^6-arene complexes of Cr(0) and Cr(I).[43] At about the same time, the first σ-organochromium compound, blood-red $CrPh_3(THF)_3$, was prepared from $CrCl_3(THF)_3$ and PhMgBr in THF at −20° (ref 44, 45). It decomposed on heating to a black solid which gave $Cr(\eta^6\text{-}C_6H_6)_2$ and $Cr(\eta^6\text{-}C_6H_6)(\eta^6\text{-biphenyl})$ on hydrolysis. More recent studies[46,47] have not altered the overall interpretation though details are still not fully understood. This aspect of chromium chemistry as well as the preparation and properties of σ-bonded organochromium compounds in general have been discussed in detail.[13] Only adducts, $CrPh_3L_3$ and, in one case, $CrPh_3L_2$, have been isolated. Decomposition to Cr(0) appears determined to a large extent by the lability of L.

Addition of L-L to $CrPh_3(THF)_3$ gives sparingly soluble $CrPh_3(L\text{-}L)(THF)$ (L-L = bpy or phen).[48] These adducts are considerably more stable than $CrPh_3(THF)_3$ and decompose at 135° (bpy) and 160° (phen).

When $CrPh_3(THF)_3$ is dissolved in neat $PPhR_2$ (R = Et, Bu) and THF removed in vacuo, five-coordinate, red-violet $CrPh_3(PPhR_2)_2$ complexes can be isolated.[49] They may be recrystallized from hexane and are monomeric in benzene. Only traces of aromatic complexes are found after refluxing for several hours in ether, benzene, or hexane even though they dissolve in THF to give $CrPh_3(THF)_3$ instantly.

A Cr(II) species, $CrPh_2(bpy)_2$, can be prepared by a direct or indirect method[50] (eq 1). It does not decompose at 80°. $CrPh_2(CHPh_2)(THF)_2$ was prepared in THF from $Cr(CHPh_2)Cl_2(THF)_2$ and 2LiPh.

$$\begin{tikzcd}
\mathrm{CrCl_2} \arrow[r, "\text{1. 2LiPh, −78° (THF)}", "\text{2. 2bpy, −20° (THF)}"'] & \mathrm{CrPh_2(bpy)_2} \\
 & (\mu = 3.22) \\
\mathrm{CrPh_2(CHPh_2)(THF)_x} \arrow[ur, "2bpy", "-\frac{1}{2}\mathrm{Ph_2CHCHPh_2}"'] &
\end{tikzcd} \qquad (1)$$

The mesityl derivatives of Cr(III) and Cr(II), in contrast, apparently do not give Cr(0) on decomposition. Violet $Cr(Mes)_3THF$ (μ = 3.74) was prepared from $CrCl_3(THF)_3$ and MesMgX in THF.[51] THF is lost in noncoordinating solvents and refluxing causes decomposition to mesitylene and Cr(III); subsequent hydrolysis did not give Cr(0) species. The authors suggest that absence of an ortho hydrogen and/or steric hindrance stabilizes $Cr(Mes)_3$ toward reduction. Intermolecular decomposition was not ruled out. Violet $Cr(Mes)_2(THF)_3$, black-violet $Cr(Mes)_2(bpy)(THF)$, and blue $Cr(Mes)Cl(THF)_2$ were reported a year later.[52] Decomposition in ether or THF also gave no Cr(0) species. Similar compounds containing the 1-naphthyl and 2-methyl-1-naphthyl ligands were reported but not well characterized.

Violet-blue $V(Mes)_3 \cdot 1.25THF$ (μ = 2.74) was prepared[53] as for the Cr analog. It is stable to 120° in vacuo and loses THF in dioxane or benzene. The solvent-free complex could not be isolated.

The existence of green diphenylmanganese[30] has been disputed.[31] If $MnPh_2$ was indeed prepared, its insolubility in ether would suggest a polymeric structure analogous to $MnMe_2$. However, as with $MnMe_2$, soluble $MnPh_2$ can be prepared in THF.[54]

Finally, several rhenium complexes containing σ-aryl groups are known.[55] Blue $RePh_3(PPhEt_2)_2$, $Re(p\text{-tolyl})_3(PPhEt_2)_2$, and $[RePh_2(PPh_3)_2]_n$ are prepared from $ReCl_3L_3$ or $Re(O)Cl_3L_2$, and orange $Re(N)Ar_2(PPh_3)_2$ (Ar = Ph, p-tolyl, o-tolyl) from $Re(N)Cl_2(PPh_3)_2$. The former are stable in refluxing benzene; the latter decompose.

3. Benzyl

Preparation of binary benzyl complexes marked the beginning of a rapid development in the area of "stable" binary alkyl complexes. Alkyl ligands such as neopentyl or trimethylsilylmethyl, stable complexes of which were soon discovered, resemble the benzyl ligand in that they too have no β hydrogen and are rather bulky. In addition to their scientific import the $M(CH_2Ph)_4$ compounds, especially the zirconium derivative, have practical potential as olefin polymerization catalysts.[56]

Tetrabenzyltitanium was prepared in solution in 1967[40,57] and isolated a year later.[58] It is most commonly prepared from $TiCl_4$ and $PhCH_2MgX$ (X = Cl, Br) in diethyl ether but variations have been studied carefully.[59-62] An interesting indirect method employing $TiMe_4$ and $B(CH_2Ph)_3$ has also been reported.[63] In general, however, $Ti(CH_2Ph)_4$ is much easier to prepare than $TiPh_4$. One important finding[60] is that some ether is necessary apparently in order to form an adduct with $TiCl_4$.

The preparations of $Zr(CH_2Ph)_4$[64,65] and $Hf(CH_2Ph)_4$[66-69] are entirely analogous to that of $Ti(CH_2Ph)_4$, while green $V(CH_2Ph)_4$ is best prepared from VCl_4 and $Mg(CH_2Ph)_2$ in pentane in the presence of a small amount of ether,[70] or in neat ether.[71] Apparently only black, crystalline $V(CH_2Ph)_4(ether)$ has been isolated.[71] Use of $PhCH_2MgCl$ gave large quantities of VCl_3 and little $V(CH_2Ph)_4$. Tetrabenzyltungsten[72a] and tetrabenzylmolybdenum[72b] have also been mentioned, but details are not yet available.

The synthesis, properties, and some reactions of $Ti(CH_2Ph)_4$ and $Zr(CH_2Ph)_4$ have been described fully[65,73,74] (Figure 1). Red $Ti(CH_2Ph)_4$ (mp 70°) and yellow $Zr(CH_2Ph)_4$ (mp 133°) are slightly soluble in aliphatic hydrocarbons, more so in aromatic hydrocarbons and ethers, and are monomeric in benzene.

Both $Ti(CH_2Ph)_4$ and $Zr(CH_2Ph)_4$ decompose in refluxing heptane in several hours (Ti ≫ Zr). The titanium compound

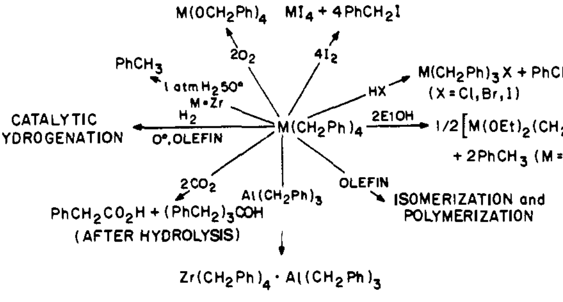


Figure 1. Some reactions of $M(CH_2Ph)_4$ (M = Ti, Zr).

yields the maximum theoretical amount of toluene which can arise from methylenic hydrogen atom transfer (2.66 mol). No deuterated toluene is produced in deuterated solvents. In the solid state both decompose to give benzene, bibenzyl, diphenylmethane, and ethylene in addition to toluene.[73] The black Zr-containing residue on deuterolysis gave a mixture of 50% H_2, 25% HD, and 25% D_2 (suggesting catalyzed H/D exchange), d_0- to d_4-toluene, and deuterated mixtures of methane and ethane, while reaction with $HgCl_2$ gave $PhCH_2HgCl$, MeHgCl, and EtHgCl, all in trace amounts.

Interestingly, $Zr(CH_2Ph)_4$ is photosensitive, more so than $Ti(CH_2Ph)_4$. Irradiation in toluene at −60° gave a brown product believed to be $Zr(H)(CH_2Ph)_2(CH_2C_6H_4CH_2Ph)$. Hydrolysis gave hydrogen, toluene, and a 1:1 mixture of *o*- and *p*-benzyltoluene. Though methanolysis with CH_3OD gave HD, infrared or ^1H NMR spectroscopy did not confirm a Zr–H bond. Photochemical activation is apparently necessary to observe rapid olefin polymerization by $Zr(CH_2Ph)_4$.[56]

Single-crystal x-ray structural determinations have been completed for the three $M(CH_2Ph)_4$ species (M = Ti, Zr, or Hf).[66,75,76] In contrast to $Sn(CH_2Ph)_4$, an essentially perfect tetrahedron with C–Sn–C angles of 108–111° and a mean Sn–C–C angle of 111°, the $M(CH_2Ph)_4$ structures are distorted with rather large variations in the C–M–C angles (e.g., 99–118° for Hf) and small mean M–C–C angles (Hf, 94°; Zr, 92°; Ti, 103°). Several authors have suggested that metal interaction with the phenyl ring contributes to their stability though no abnormal ^1H NMR spectral features support this proposal. The structure of $V(CH_2Ph)_4$ is also a distorted tetrahedron as suggested by the well-resolved ESR spectrum at room temperature.[70]

Several adducts of tetrabenzyl species are known. $Ti(CH_2Ph)_4(bpy)$ has been isolated at room temperature[35,63] and adducts with TMEDA, TMPDA, TMMDA, and py are formed in solution.[35] At low temperature $Ti(CH_2Ph)_4(ether)_2$ crystallizes from ether.[63] Adducts of $Zr(CH_2Ph)_4$ with bipyridyl[67,73,77] and py, THF, thioxane, and other donors[77] have also been isolated. An ^1H NMR study[67–69] of Lewis base interactions with $Zr(CH_2Ph)_4$ and $Hf(CH_2Ph)_4$ has shown that (i) only monoadducts form for L = py, quin, PMe_3, or THF; (ii) the equilibrium constant for pyridine adduct formation in chlorobenzene is ca. 13 for $Zr(CH_2Ph)_4$ and ca. 460 for $Hf(CH_2Ph)_4$; (iii) no adducts form with NR_3 (R = Et, Pr, Bu, or Ph), TEEDA, diethyl ether, dioxane, PPh_3, $P(OMe)_3$, $P(OEt)_3$, cyclooctene, cyclohexene, or 1,1-diphenylethylene; and (iv) bipyridyl forms insoluble $M(CH_2Ph)_4(bpy)$. Clearly steric factors play an important role.

Reaction of $TiCl_3(THF)_3$ with $PhCH_2MgCl$ in ether at −45° gives a brown solution which may contain $Ti(CH_2Ph)_3$ as suggested by reaction with $3.5I_2$ to give TiI_4 and $3PhCH_2I$.[78] When the temperature of the initial mixture rose to 20° a red color developed, ethane, methane, and smaller amounts of ethylene, propane, and pentane were evolved, and $Ti(OEt)_2(CH_2Ph)_2(ether)_2$ was subsequently isolated. The solvent-free form, $[Ti(OEt)_2(CH_2Ph)_2]_2$, was prepared from $Ti(CH_2Ph)_4$ and 2 mol of ethanol.[58,65]

The reaction between $TiCp_2Ph_2$ and $2LiCH_2Ph$ reportedly gives $Ti(CH_2Ph)_2$.[79] The authors suggested a polymeric solid-state structure. It dissolved in tetrahydrofuran in which it reacted with HCl to give 2 mol of toluene.

Neither $Cr(CH_2Ph)_4$ nor $Cr(CH_2Ph)_3$ has been isolated. ESR evidence for the former was obtained[29,80] while the latter probably exists at low temperature.[81] On hydrolysis at 20° the mixture from the −78° reaction of $3PhCH_2MgCl$ and $CrCl_3(THF)_3$ gave H_2, toluene, bibenzyl, 2-benzyltoluene, and $[Cr(\eta^6\text{-2-benzyltoluene})(\eta^6\text{-toluene})]^+$, isolated as its tetraphenylborate salt.

The dimeric complexes, $M_2(CH_2Ph)_6$(M = Mo, W), are probably structurally similar to $Mo_2(CH_2SiMe_3)_6$[82] (section 4, below). Preparative details have not yet been published.

Finally, $Mn(CH_2Ph)_2$ was prepared in THF but not isolated.[32]

4. Neopentyl, Trimethylsilylmethyl, and Related Alkyls

Neopentyl and trimethylsilylmethyl ligands have been used to prepare what is now the most extensive class of binary metal alkyls.

The group 4 $M(CH_2CMe_3)_4$ complexes are usually prepared from neopentyllithium and MCl_4 in an ethereal solvent and red-purple $Cr(CH_2CMe_3)_4$ by air oxidation or disproportionation of $[Cr(CH_2CMe_3)_4]^-$ in hydrocarbons or ether.[29,80,83–85] (In THF $Cr(CH_2CMe_3)_3(THF)_3$ does not readily disproportionate.[28]) The pale yellow to colorless group 4 complexes are all volatile, low-melting solids which sublime in vacuo without decomposition. Attempted preparation of $V(CH_2CMe_3)_4$ from either VCl_4 or $VOCl_3$ and neopentyllithium in saturated hydrocarbons gave brown solutions whose ESR spectra were not consistent with its formation.[84]

Corresponding $M(CH_2SiMe_3)_4$ complexes have been prepared for M = Ti, Zr, Hf, and Cr, and also for M = V by analogous methods.[83,86–89] The group 4 complexes are liquids at room temperature. The green vanadium complex is somewhat unstable at room temperature in contrast to the group 4 complexes. $Cr(CH_2SiMe_3)_4$ is remarkably inert toward water, dilute mineral acids, amines, phosphines, alkenes, phenylacetylene, and CO at 100° and 200 psi, but reacts with oxygen. In contrast, $V(CH_2SiMe_3)_4$ decomposes in aqueous solutions, alcohols, and chlorinated solvents and is oxidized to $V(O)(CH_2SiMe_3)_3$ on passage through a cellulose column, yet it does not react under mild conditions with CO, alkenes, acetylene, or phosphines.

Related MR_4 species such as $Cr(CH_2CMe_2Ph)_4$ and $Cr(CH_2CPh_3)_4$,[29,80] $Zr(CH_2SiMe_2Ph)_4$,[87] and $Ti(CH_2SiMe_2Ph)_4$[90] have been mentioned. A crystal structure[91] of $Cr(CH_2CMe_2Ph)_4$ clearly shows the dense packing around the metal which is assumed to be at least partly responsible for its chemical stability. It is a slightly distorted tetrahedron with Cr–C distances from 2.01 to 2.07 Å.

Because the Cr(IV) oxidation state is rather unusual, the ESR and electronic spectra of CrR_4 species have been thoroughly studied.[28,29,80,92] Several ESR signals are generally observed, possibly because the alkyls cannot rotate about the metal–carbon bond. Both electronic and ESR spectra suggest a distorted tetrahedral symmetry.

Attempts to prepare binary $-CH_2CMe_3$ or $-CH_2SiMe_3$ complexes from $NbCl_5$, $TaCl_5$, $MoCl_5$, and WCl_6 gave unanticipated results, probably in part because more than four of these bulky ligands on a single metal is sterically unfavorable. The niobium and tantalum reactions gave both bridging and terminal carbene complexes (see section II.A.5), probably by α-hydrogen abstraction.

Attempts to prepare $-CH_2SiMe_3$ complexes of Mo(V) or W(VI) employing Me_3SiCH_2MgCl gave the dimers, $M_2(CH_2SiMe_3)_6$, which are stable in air for a short time and sublime in vacuo at 120° (ref 83, 88). A crystal structure[82] of

$Mo_2(CH_2SiMe_3)_6$ shows the following essential features: (i) a short (2.167 Å) Mo-Mo distance indicates a multiple metal-metal bond; (ii) each molybdenum has a distorted tetrahedral coordination and the three alkyl groups on one atom are staggered relative to the three on the second; (iii) the Mo-CH_2-Si angle (121°) and the Mo-Mo-CH_2 angle (101°) are probably a consequence of the mutual repulsion of the bulky trimethylsilyl groups; and (iv) the mean Mo-CH_2 distance is 2.131 Å. The tungsten analog is isostructural.

To avoid low yields the analogous $Mo_2(CH_2CMe_3)_6$ compound must be prepared with neopentyllithium instead of the Grignard reagent.[84] Though it is sufficiently volatile to sublime (130°), it is slightly more unstable than the $-CH_2SiMe_3$ analog and decomposes at this temperature.

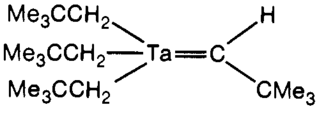
All complexes in this section have been fully examined by infrared, ^1H NMR, or ESR (for V and Cr) spectroscopy, but only qualitative reactions reported. Unfortunately, the large ligands hinder a reagent's approach to the metal and thereby limit to some extent reaction under conditions where the complex remains intact. Ironically, this is probably one reason why the complexes can be prepared in the first place.

5. *Alkylidenes*

Neopentyl and CH_2SiMe_3 alkylating agents react with $NbCl_5$ and $TaCl_5$ to give compounds containing carbene ligands probably because more than four bulky alkyl groups cannot fit around a single metal atom.

Addition of MCl_5 to 5.5 mol of Me_3SiCH_2MgX in ether did not give $M(CH_2SiMe_3)_5$ (M = Nb or Ta) but $[M(CH_2SiMe_3)_2(CSiMe_3)]_2$.[83,84] These red (Nb) or orange (Ta) complexes do not sublime in vacuo though they are soluble in pentane and decompose only at their melting points, 152 and 170°, respectively. Formulation of the Nb complex has been confirmed by a crystal structure[93] shown schematically in Figure 2. The two crystallographically independent dimers do not differ significantly. The metals and bridging carbon atoms lie in a plane but neither the Nb-C(bridging)-Si angles nor the Nb-C(bridging) distances are identical in a given molecule. Nevertheless, the Nb-C-Nb-C ring can be described as quasi-aromatic, a fact which explains the diamagnetism of these complexes and possibly also why they do not readily react with NO, CO, tertiary phosphines, amines, or alkenes. Their mechanism of formation is unknown and neopentyl analogs were not obtained.

The attempted preparation of $Ta(CH_2CMe_3)_5$ from $Ta(CH_2CMe_3)_3Cl_2$ and 2 mol of $LiCH_2CMe_3$ in pentane gave 2 mol of LiCl, 1 mol of neopentane, and very soluble, orange, crystalline $Ta(CH_2CMe_3)_3(CHCMe_3)$.[94] Its ^1H NMR, mass spectrum, and molecular weight are consistent with formulation as



$$(Me_3CCH_2)_3Ta{=}C(H)CMe_3$$

Hydrolysis with 5 mol of DCl produced 3.7 mol of a mixture of three parts neopentane-d_1 and one part neopentane-d_2 while ^{13}C NMR confirmed the presence of a carbene-carbon with a 250-ppm chemical shift. Labeling experiments suggest formation via $Ta(CH_3CMe_3)_5$ by intramolecular α-hydrogen abstraction. An exactly analogous reaction gives wine-red $Nb(CH_2CMe_3)_3(CHCMe_3)$.[95] The former is extraordinarily stable thermally, the latter considerably less so. Their isolation demonstrates clearly that, under some conditions, (i) alkylidene complexes are stable and (ii) intramolecular α-hydrogen abstraction is a viable mode of "decomposition" of binary alkyl complexes.

Interestingly, elimination of a second mole of neopentane to give the carbon analog of $[M(CH_2SiMe_3)_2(CSiMe_3)]_2$ (vide supra), i.e.,

$$M(CH_2CMe_3)_3(CHCMe_3) \xrightarrow{-C_5H_{12}} 0.5[M(CH_2CMe_3)_2(CCMe_3)]_2$$

does not occur readily despite the fact that lithium reagents react with $M(CH_2CMe_3)_3(CHCMe_3)$ to give $M(CH_2CMe_3)_3[C(CMe_3)(Li{\cdot}L_x)]$ (L_x = N,N′-dimethylpiperazine, for example),[94] i.e., the neopentylidene α proton is more acidic than a neopentyl α proton. Failure to isolate $M(CH_2SiMe_3)_3(CHSiMe_3)$ may possibly be ascribed to the greater acidity of protons α to silicon vs. α to carbon.

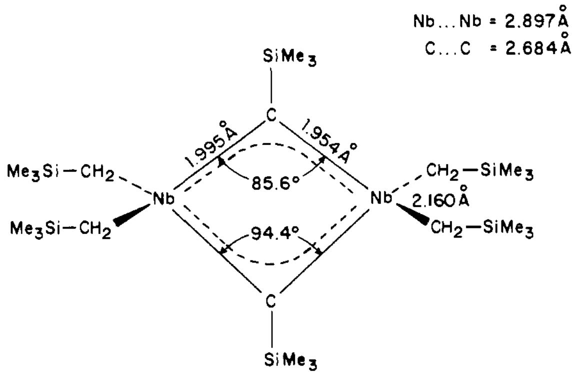
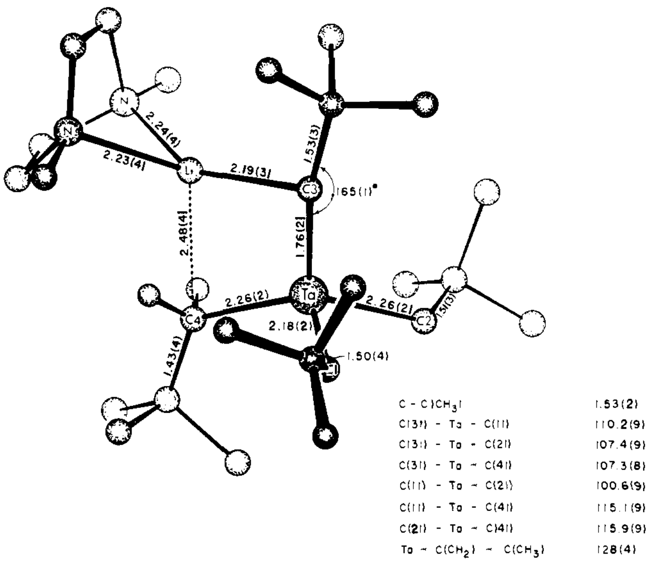


Figure 2. The structure of $[Nb(CH_2SiMe_3)_2(CSiMe_3)]_2$ (ref 93).



C – C(CH3)	1.53(2)
C(31) – Ta – C(11)	110.2(9)
C(31) – Ta – C(21)	107.4(9)
C(31) – Ta – C(41)	107.3(8)
C(11) – Ta – C(21)	100.6(9)
C(11) – Ta – C(41)	115.1(9)
C(21) – Ta – C(41)	115.9(9)
Ta – C(CH2) – C(CH3)	128(4)

Figure 3. The structure of $Ta(CH_2CMe_3)_3[C(CMe_3)(Li{\cdot}$*N,N′*-dimethylpiperazine)].

A crystal structure of the lithiated Ta species has been completed[96] (see Figure 3). The extraordinarily short tantalum to "carbene"-carbon distance (1.76 Å) and large Ta-C-CMe_3 angle suggest that this compound should be viewed as a "carbyne" complex analogous to group 6 carbyne complexes.[97]

6. *Other Alkyls*

a. Bulky Alkyls

Complexes of the type M(1-norbornyl)$_4$ where M = Ti, Zr, Hf, V, and Cr (also Mn, Fe, and Co) were prepared from the metal halides and 1-norbornyllithium in pentane.[98] Disproportionation to yield M(IV) species was the rule when lower valent halides were used. Chromium (2,3,3-trimethylbicyclo[2.2.1]hept-1-yl)$_4$ could also be prepared but with 2,2,3-trimethylbicyclo[2.2.1]hept-1-yl only CrR_3 (61% yield) resulted. Ligand interrepulsions must be too large in CrR_4 in this case. All are pentane-soluble, monomeric, and pass through an alumina column unchanged. The authors attribute their thermal stability ($t_{1/2}$ = 29 h at 100° for TiR_4) to the fact that β-hydrogen abstraction is unfavorable (unsaturation at a bridgehead carbon would result) and their chemical stability (M = Ti, V, or Cr) to the ligands' close packing around these relatively small metals. It is also interesting to note 1-norbornyl has no α proton which would allow decomposition by an α-abstraction process. ESR[98-100] and preliminary x-ray data (for Cr(1-norbornyl)$_4$) suggest tetrahedral structures.

Apparently only three $CH(SiMe_3)_2$ ligands can fit conveniently about a first-row transition metal. Paramagnetic $M[CH(SiMe_3)_2]_3$ species (M = Ti, V, Cr) have been isolated[101a] and at least the Cr complex is quite stable thermally; it decomposes at ca. 80°. Excess $LiCH(SiMe_3)_2$ reacts with MCl_4 (M = Zr, Hf) in ether to give only $M[CH(SiMe_3)_2]_3Cl$ while 1 mol reduces $TiCp_2Cl_2$ to $[TiCp_2Cl]_2$. $CH(SiMe_3)_2$ must be about the size of $N(SiMe_3)_2$ for which many three-coordinate complexes are known.[101b]

Though the *tert*-butyl ligand is very susceptible in most circumstances to β-hydrogen abstraction, $Cr(CMe_3)_4$ can be prepared in 60% yield from $Cr(OCMe_3)_4$ and $LiCMe_3$ in pentane.[28] It can be chromatographed on alumina and sublimes at 10^{-4} mm. The activation energy for decomposition ($t_{1/2}$ = 4.5 min at 70° in heptane) measured over the range 55 to 80° was 29 ± 3 kcal/mol. At 80° the decomposition products were isobutane and isobutylene (6.5:1) containing small amounts of methane, ethane, and propane. Its stability is attributed to the fact that the methyl groups are tightly packed and cannot orient properly for β-hydrogen abstraction to occur.

Colorless Ti(1-adamantyl)$_4$ was prepared recently in 18% yield from $TiCl_4$, Na, and 1-chloroadamantane in refluxing cyclohexane.[102a] Considerable biadamantane was also obtained, consistent with a radical reaction. The extraordinary thermal stability of Ti(1-adamantyl)$_4$ (mp 233-235°; "the compound proved difficult to decompose with HNO_3-HF-H_2O_2 mixtures at 170° when analyzing for the metal") combined with the fact that the adamantyl radical is fairly long-lived (ref 13 in ref 102a) suggests that homolytic metal-carbon bond cleavage is not a common *primary* decomposition step (see section VI.E). β-Hydrogen abstraction is unfavorable for reasons analogous to those stated for 1-norbornyl; 1-adamantyl also has no α hydrogen.

b. "Unstable" Alkyls

Except for special cases (e.g., $Cr(CMe_3)_4$) and in monoalkyl complexes with an 18 valence-electron count (e.g., $Mn(CO)_5Et$), complexes of alkyl groups containing a β-hydrogen atom are accessible only at low temperature or in coordinating solvents. For example, TiR_4 species where R = Cy, Bu, CMe_3, Pr^i, Pr, and Et can be prepared without accompanying reduction to Ti(III) by adding $Ti(OCMe_3)_4$ to RMgX at low temperatures.[59] The CrR_4 species where R = Pr^i, s-Bu, Bu, and cyclohexylmethyl, prepared as for $Cr(CMe_3)_4$, are "more or less stable between −78° and room temperature" in pentane.[28] For R = Bu and cyclohexylmethyl, CrR_4 appeared stable for several hours at 0° in pentane. Decomposition rates of MnR_2 in THF[32] are almost certainly moderated by formation of $MnR_2(THF)_2$. They vary in the order R = $Pr^i > CMe_3 > Et > Pr \sim Bu \gg Me \sim CH_2CMe_3 \sim CH_2Ph$. ("$MnPr_2$" decomposes 10% in 2 h at 25°.) Though decomposition of long-chained alkyl complexes produced in situ may be accelerated by metal salts, reduced metal complexes, etc., the basic contention concerning their instability appears sound. Exceptions, where the valence-electron count is less than 18, will probably have a crowded coordination sphere similar to that in $Cr(CMe_3)_4$.

c. "Mixed" Alkyls

A few complexes containing more than one type of alkyl are known. Not unexpectedly, properties of the mixed binary complexes are roughly intermediate between those of the parent species.

Exchange between $TiMe_4$ and BPh_3 or $B(CH_2Ph)_3$ at −78° in diethyl ether yields $TiMe_2Ph_2$ or $TiMe(CH_2Ph)_3$, respectively, and BMe_3.[63] ($TiMe(CH_2Ph)_3$ has also been prepared from $Ti(CH_2Ph)_3Cl$ and MeMgI.[65]) In the latter case raising the temperature to −30° caused complete exchange to give $Ti(CH_2Ph)_4$. The reaction with BPh_3 was not altered by changing the reactant ratio. One suggested mechanism

$$TiMe_4 + BPh_3 \rightleftharpoons [TiMe_3]^+[BMePh_3]^- \rightleftharpoons TiMe_3Ph + BMePh_2 \rightleftharpoons \text{etc.}$$

should be compared with the proposed mechanism of methyl exchange between $TiMe_4$ and $AlMe_3$ in the presence of ether:[102b]

$$TiMe_4 + AlMe_3 \rightarrow [TiMe_3]^+[AlMe_4]^-$$

The reaction of $Cr(CHPh_2)Cl_2(THF)_2$ with phenyllithium to give $Cr(CHPh_2)Ph_2(THF)_2$ was briefly mentioned[50] as was a bipyridyl adduct.

B. Anionic

Most "anionic" metal alkyls contain one or more alkali metal counterions. Since lithium alkyls contain bridging alkyl groups, it is not surprising that the "anionic" complexes contain the Li-R-M arrangement. The truly anionic complex, $[Li(THF)_4]^+[TaPh_6]^-$, probably exists because a structure containing Li-Ph-Ta bonds is sterically unfavorable.

1. Methyl

Addition of methyllithium to $TiMe_4$ in ether followed by 2 mol of dioxane gives a precipitate, $Li[TiMe_5]$·2diox.[103,104] Conductivity measurements in THF favor an ionic formulation but the manner in which dioxane is bound is uncertain. Similarly, $TiMe_4$ and LiPh or $LiCH_2Ph$ (LiR) gave $Li[TiRMe_4]$·2dioxane, and $TiMe_2Ph_2$ and LiPh, $Li[TiMe_2Ph_3]$·2dioxane. All decompose at −20° to 0°.

Reaction of $ZrCl_4$ with >6 mol of methyllithium in ether–toluene gives $Li_2[ZrMe_6]$.[105] The bright yellow crystals are stable under nitrogen at 0° for several hours and dissolve in ether, tetrahydrofuran, and toluene, but not in aliphatic hydrocarbons. In toluene, alcoholysis produced only methane (6 mol per Zr). A structure was not proposed but may well contain Li-Me-Zr bridges as found in $Li_3[CrMe_6]$·3(solvent) (vide infra). Some bridging structure is probably retained even in coordinating solvents, though $[ZrMe_6]^{2-}$ does not seem unreasonable.

Similar anionic niobium and tantalum complexes, $[MMe_n]^{5-n}$ (n = 6 or 7), are probably formed in ether from appropriate quantities of $TaMe_3Cl_2$ or $NbMe_2Cl_3$ and methyllithium.[22] However, the ^1H NMR spectrum of $Li_2[TaMe_7]$ in THF suggests equilibria between at least two unidentified species and methyllithium. Ether solutions are remarkably stable compared with those of $TaMe_5$ or $NbMe_5$ yet methyllithium is readily lost on addition of dmpe and MMe_5(dmpe) isolated.

The chromium-methyl system has been studied most extensively so far. Reaction between $CrCl_3$ and 6LiMe in ether at −18° gives $Li_3[CrMe_6]$, isolable as blood-red Li_3CrMe_6·3dioxane on addition of dioxane.[106] It is insoluble in hexane and benzene (it slowly decomposes in these solvents) but is soluble and stable in ether and dioxane in which it is monomeric and apparently undissociated. Its reactions with H_2O and I_2 give 6 mol of methane and 6 of methyl iodide, respec-

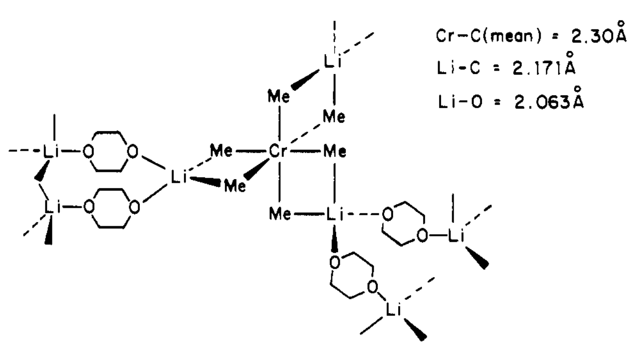


Figure 4. A schematic drawing of $Li_3CrMe_6(diox)_3$.

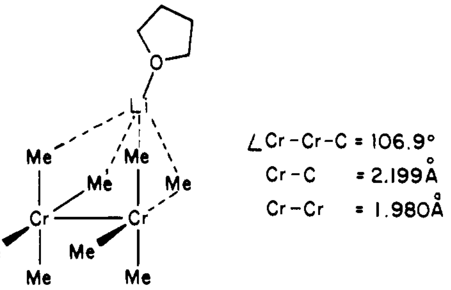


Figure 5. Partial schematic structure of $[Li_2CrMe_4(THF)_2]_2$.

tively. Its structure[107] is shown schematically in Figure 4. Six methyl groups are disposed in a slightly distorted octahedral arrangement around Cr, and each tetrahedral lithium atom is surrounded by two methyls and two dioxanes. The dioxanes bridge to lithiums in other molecules. The Ti and Zr complexes discussed above are most likely structurally related.

In ethers Li_3CrMe_6 slowly decomposes to give a dimeric Cr(II) complex:[106]

$$2Li_3CrMe_6 \xrightarrow{R_2O} [Li_2CrMe_4(OR_2)_2]_2 + 2LiMe + 2\text{"}Me\cdot\text{"}$$

The dimer may also be prepared directly from $CrCl_2$ and methyllithium or from $Cr_2(\eta^3\text{-}C_3H_5)_4$ and 8LiMe in THF.[108] Its reduced paramagnetism ($\mu = 0.57$) suggests a Cr–Cr bond. The structure[109] of $[Li_2CrMe_4(THF)_2]_2$ is partially shown in Figure 5. Each of the four equivalent faces of the tetragonal prismatic unit composed of eight methyl groups and two joined chromium atoms is capped with a lithium atom to which a THF molecule is also bound. The authors postulate a quadruple Cr–Cr bond.

$MoCl_3(THF)_3$ is reduced by 5LiMe to give $Li_2MoMe_4(THF)_2$ and 0.5 mol of *ethane*, according to the authors.[110a] (Li_3MoMe_6 is apparently not isolable.) $Li_2MoMe_4(THF)_2$ is a diamagnetic dimer analogous to $[Li_2CrMe_4(ether)_2]_2$ (vide supra). This is confirmed by an x-ray structure[110d] where Mo–Mo = 2.148 Å and Mo–C(mean) = 2.29 Å.

Also in this class is $[Li_2Cr(C_4H_8)_2(ether)_2]_2$ (see section II.B.3 and Figure 6).[111] The metallocyclic rings are staggered with Cr–Cr = 1.975 Å. The Cr–CH_2 distances and angles are variable.

The only other "anionic" methyl complex is $Li[MnMe_3]$.[31] Few details concerning its preparation and properties are available.

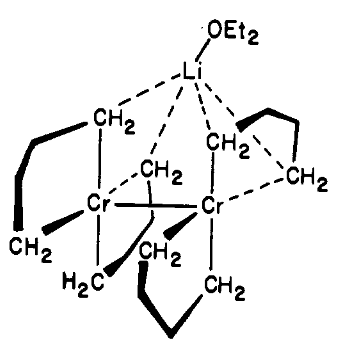


Figure 6. Partial schematic structure of $[Li_2Cr(C_4H_8)_2(Et_2O)_2]_2$.

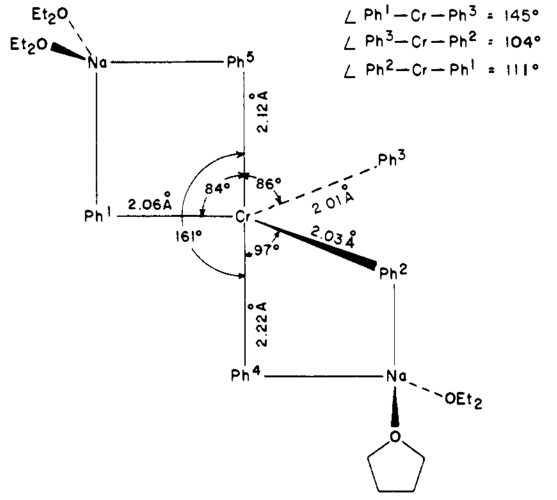


Figure 7. A schematic drawing of $Na_2CrPh_5(ether)_3(THF)$.

2. Phenyl

The reaction of LiPh with $CrCl_3$ in ether[112] simply gives metathesis in contrast to reduction to Cr(0) usually observed with Grignard reagents. The orange crystalline product, isolated in high yield, has the formula $(LiPh)_3CrPh_3(ether)_{2.5}$. It is also formed starting with $CrBr_3$, $CrCl_3(py)_3$, $Cr(acac)_3$, and Cr(II) salts, disproportionation occurring in the latter instance.[113] Hydrolysis with water gives 6 mol of benzene but some biphenyl is formed on reaction with iodine:

$$(LiPh)_3CrPh_3(ether)_{2.5} + 4.5I_2 \rightarrow 3LiI + CrI_3 + 3PhI + 1.5Ph_2$$

Somewhat surprising also is its reaction with molecular hydrogen to give postulated Li_3CrHPh_5 and $Li_3Cr_2H_3Ph_6$. Its molecular weight in benzene is close to theory initially, but ether is gradually lost and $(LiPh)_3CrPh_3$ can be isolated as a yellow powder. The magnetic moment (3.61) is characteristic of octahedral Cr(III) and its structure is probably similar to that of $Li_3CrMe_6(diox)_3$ (cf. the structure of $Na_2CrPh_5(ether)_3(THF)$ below).

Lower members of the $M_{x-3}CrPh_xS_y$ family (x = 4, 5, or 6, M = Na or Li, S = an ether) have also been studied. The blue-green product resulting from the reaction of NaPh with $CrCl_3$ is $Na_2CrPh_5(ether)_3$,[114] analogous to the lithium derivative reported several years earlier.[115] (Yellow Na_3CrPh_6 is unstable toward loss of NaPh.) It is monomeric in ether (ebullioscopy), has a magnetic moment of 3.66, and gives olive-green $Na_2CrPh_5(bpy)_2$ (μ = 3.90) with bipyridyl. A crystal structure[116] of $Na_2CrPh_5(ether)_3(THF)$ reveals a greatly distorted trigonal-bipyramidal geometry about Cr with each Na interacting with two phenyl rings (Figure 7).

The lowest members (x = 4, M = Li, Na) are prepared by redistribution reactions[117] (ether molecules omitted):

$$4Na_2CrPh_5 + CrCl_3 \rightarrow 5NaCrPh_4 + 3NaCl$$

$$2Li_3CrPh_6 + CrCl_3 \rightarrow 3LiCrPh_4 + 3LiCl$$

Each can be characterized as its blood-red dimethoxyethane adduct, $MCrPh_4(dme)_4$ (μ = 3.85 for M = Na, 3.65 for M = Li). The magnetic moments appear to rule out formulation as $[M(dme)_4]^+[CrPh_4]^-$; octahedral Cr(III) with two dme ligands and two bridging phenyl groups to $Na(dme)_2$ is more plausible.

All members of the Cr(III) class react with $CrCl_3$ to yield Cr(II) complexes under proper conditions:[118]

$$4Na_2CrPh_5(ether)_3 + CrCl_3(THF)_3 \rightarrow 5NaCrPh_3(ether)_{1.5} + \tfrac{5}{2}Ph_2 + 3NaCl$$

$$2Li_3CrPh_6(ether)_{2.5} + CrCl_3(THF)_3 \rightarrow 3LiCrPh_3(ether)_{1.5} + \tfrac{3}{2}Ph_2 + 3LiCl$$

These are brown-black, soluble in THF, benzene, diglyme, and diethyl ether, and react characteristically with H_2O, $HgCl_2$ and I_2. Their reduced magnetic moments (ca. 0.6–0.8) and dimeric character (molecular weight studies) indicate they probably are structurally similar to $[Li_2CrMe_4(THF)_2]_2$.

Finally, a monomeric, anionic Cr(II)–phenyl complex has been isolated:[50]

$$\begin{tikzcd} Cr(CHPh_2)Ph_2\ (in\ situ) + 2LiPh \arrow[r, "THF-ether"'] & Li_2Cr(CHPh_2)Ph_4 \arrow[d, "-0.5Ph_2CHCHPh_2"'] \\ & Li_2CrPh_4(THF)_4 \end{tikzcd}$$

It can also be prepared from $CrCl_2(THF)_2$. The yellow crystalline complex is stable in an inert atmosphere to approximately 90°. Its magnetic moment (4.73) is characteristic of a high-spin d^4 species and suggests it is not a member of the dimeric class, $[Li_2CrR_4S_2]_2$, but the sole member of a third class of "anionic" organochromium species. Apparently the large phenyl groups prevent dimerization.

A molybdenum species, $(LiPh)_3MoPh_3(ether)_3$, is formed in 20% yield on reaction of $MoCl_5$ with 10 mol of LiPh in ether at −30° (ref 119). The yellow crystals, obtained from a dark red reaction mixture, dissolve in ether, benzene, THF, or butyl ether to again give a red color which is believed that of a species formed by loss of LiPh. Hydrolysis produced ether and benzene in a 1:2 ratio while thermal decomposition left a black, crystalline, ether-soluble residue which was not identified. Its "anomalous" reaction with $HgCl_2$, viz.

$$(LiPh)_3MoPh_3 + 6HgCl_2 \rightarrow 3PhHgCl + 1.5Hg_2Cl_2 + 1.5C_6H_5\text{–}C_6H_5 + MoCl_3 + 3LiCl$$

was taken as evidence against the "$Li_3MoPh_6(ether)_3$" formulation suggested by other authors.[120]

An apparently analogous tungsten complex was prepared from WBr_5 and excess LiPh in ether at 0–10° (ref 121). It is a finely crystalline, black powder which gives deep violet benzene and ether solutions. Reformulation as $(LiPh)_4WPh_2(ether)_4$ was suggested[122] based on titration[123] and flame photometry.[124] It reacts with 2 mol of hydrogen reportedly to give $WH(LiPh)_4$.[125,126]

Anionic vanadium complexes have also been reported. For example,[127]

$$10LiPh + VCl_3(THF)_3 \xrightarrow{THF} (LiPh)_4VPh_2(ether)_4$$

As for Cr, the Grignard reagent gives zerovalent species.[128] The permanganate-colored crystalline product (μ = 3.85), soluble in ether and benzene, was later prepared from VCp_2Ph and 7LiPh in 66% yield.[129] With only 2 mol of LiPh in the latter reaction, $(LiPh)VPh_2(ether)$ is formed. A third complex was also reported:

$$VCp_2 + 7LiPh \rightarrow 2LiCp + (LiPh)_5VPh_2(ether)_5$$

Two niobium complexes have been reported:[130,131]

$$NbBr_5 + 8LiPh \xrightarrow{ether} (LiPh)_3NbPh_4(ether)_3 \quad (\mu = 1.66)$$

$$NbBr_5 + 9LiPh \xrightarrow[24\ h]{ether} (LiPh)_4NbPh_2(ether)_{3.5} \quad (\mu = 1.81)$$

Both are black-violet, thermally unstable, and soluble in benzene or dioxane; they do not conduct in dioxane. Niobium oxidation states 4+ and 2+, respectively, but no definite structures, were proposed.

Black-violet $(LiPh)_4TaPh_2(ether)_{3.5}$ was prepared in an identical manner[132a] (μ = 1.68). A bright green intermediate, $(LiPh)_3TaPh_3(ether)_{2.5-3}$, was also isolated.

In another report[132b] the authors draw a distinction between magnetically "normal" and magnetically "abnormal" complexes of the type $(LiPh)_4MPh_x(ether)_y$ on the basis of oxidation products with oxygen. The complexes of Nb, Ta, and W give triphenylene while pure LiPh and those of V and Cr do not. They inferred the former contain ortho-disubstituted phenyl groups, a hypothesis supported by the ^1H NMR spectrum of the W complex in which an A_2B_2 pattern characteristic of an ortho-disubstituted phenyl group appears. They suggested the Nb, Ta, and W complexes therefore be reformulated as M(IV) species, $(LiPh)_4M(C_6H_4)_2$. The manner in which phenylene coordinates was not discussed, but it could conceivably bridge two metals as in $Ni_2(o\text{-}C_6H_4)_2(PEt_3)_4$.[133]

The only truly anionic phenyl complex is $[TaPh_6]^-$ (ref 134). Addition of 5 mol of LiPh (17.8% in a benzene:ether solvent, 77:23) to $TaCl_5$ in benzene at ca. 20° followed by filtration, and addition of tetrahydrofuran gave crystals of orange, light-sensitive $[Li(THF)_4]^+$ $[TaPh_6]^-$. Other reactant ratios or temperatures gave lower yields (or none at all) though this could at least partially be a function of product solubility. Salts containing $[NEt_4]^+$ and $[AsPh_4]^+$ were prepared by metathesis reactions. All have ^1H NMR spectra consistent with their formulation and conduct in tetrahydrofuran or acetonitrile. Isolation of $[TaPh_6]^-$ is surprising since the metal is commonly reduced in systems of this type. Reactant ratio, order of addition of reagents, and mixed solvent are probably all crucial in preventing reduction. $[TaPh_6]^-$ probably forms directly but disproportionation of a reduced species is not unreasonable, especially in view of the low isolated yield.

$WH(LiPh)_4$,[125,126] Li_3CrHPh_5,[113] and $Li_3Cr_2H_3Ph_6$[113] are the postulated products of the reaction of molecular hydrogen with the corresponding anionic phenyl complexes (vide supra). Perhaps the best characterized complexes of this type are diamagnetic $Li_2MoPh_2H_2$[110b] and $Li_4MoPh_2H_2Me_2(diox)_2$[110c]:

$$5Li_3MoPh_6 + MoCl_3(THF)_3 \rightarrow 6Li_2MoPh_2H_2 + 3C_6H_5\text{–}C_6H_5 + 3LiCl + 12\text{"}C_6H_4\text{"}$$

$$Li_2MoPh_2H_2 + 2LiMe{\cdot}diox \rightarrow Li_4MoPh_2H_2Me_2(diox)_2$$

Apparently ortho-hydrogen abstraction (see section VI.A) gives dehydrobenzene which can be trapped by anthracene to give triptycene.[110b] Both complexes were characterized by hydrolyses and by ^1H NMR in which the peaks at τ 8.05 and 8.70, respectively, were assigned to the proposed bridging hydride ligands. Further investigation of these species, including an x-ray structure, would be relevant to understanding the peculiarities of MPh_x species, their mode of decomposition, and metal reduction.

No group 4 or 7 phenyl complexes analogous to those described in this section have been reported. Ether-insoluble $LiMnPh_3$ (as well as the analogous p-tolyl and p-anisyl complexes) was reported in an early work,[31] but preparation and properties have not been described in detail.

3. Other Alkyls

Dark blue $[Cr(CH_2CMe_3)_4]^-$ (ref 29, 83) and blue-green $[Cr(CH_2SiMe_3)_4]^-$ (ref 83, 88) are the products of reaction of $CrCl_3(THF)_3$ in tetrahydrofuran with the appropriate lithium reagent. They are stable only in THF, and attempts to isolate crystalline salts by addition of large cations failed. They are

TABLE I

		Cr–N		
	Cr–C	Cis to C	Trans	Ref
$[\mathrm{CrPh_2(bpy)_2}]^+\mathrm{I}^-$	2.087 (4)	2.087 (4)	2.147 (4)	138a
$[\mathrm{Cr(}o\text{-}\mathrm{CH_3OC_6H_4)_2(bpy)_2}]^+\mathrm{I}^-$	2.101 (12)	2.071 (10)	2.156 (10)	141, 142
$[\mathrm{Cr[CH_2SiMe_3]_2(bpy)}]^+\mathrm{I}^-$	2.107 (12)	2.103 (7)	2.156 (7)	139, 140

readily oxidized in solution by air to $\mathrm{CrR_4}$ from which they may be regenerated polarographically or with sodium amalgam. Half-wave reduction potentials with $[\mathrm{NBu_4}]^+\mathrm{I}^-$ as the supporting electrolyte in ethanol are −1.28 V for $[\mathrm{Cr(CH_2SiMe_3)_4}]^-$ and −1.65 V for $[\mathrm{Cr(CH_2CMe_3)_4}]^-$ vs. the saturated calomel electrode. Electronic properties suggest that these are two of the few examples of tetrahedral Cr(III).

A chromium complex containing the bidentate alkyl $-(\mathrm{CH_2})_4-$ has been prepared:[135]

$$\mathrm{CrCl_3} + 3\mathrm{LiC_4H_8Li\text{-}dioxane} \xrightarrow{\text{ether}} \mathrm{Li_3Cr(C_4H_8)_3(diox)_{2.5}}$$
$$(\mu = 3.9)$$

It is believed analogous to $\mathrm{Li_3CrMe_6(diox)_3}$ as suggested by physical properties and decomposition to $[\mathrm{Li_2Cr(C_4H_8)_2(ether)_2}]_2$. A structural determination of the latter showed it to be a member of the $[\mathrm{Li_2CrR_4S_2}]_2$ family (S = solvent; see section II.B.1). A preparation employing $\mathrm{LiC_5H_{10}Li}$ gave another member of this family, $[\mathrm{Li_2Cr(C_5H_{10})_2(LiBr)(ether)_2}]_2$, directly.

Other anionic phenyl chromium species have been isolated with pyrrolyl, diphenylamido, or dicyclohexylphosphido ligands[136] (eq 2). The first is in the $\mathrm{MCrR_4}$ class (M = e.g., Li);

$$\mathrm{CrPh_3(THF)_3}\begin{cases} + \mathrm{LiC_4H_4N} \longrightarrow \mathrm{LiCrPh_3(C_4H_4N)(THF)_3} \\ \qquad\qquad (\mu = 3.78) \\ + 2\mathrm{KNPh_2{\cdot}3diox} \xrightarrow{-\frac{1}{2}\mathrm{Ph_2}} \mathrm{K_2CrPh_2(NPh_2)_2(THF)_2} \\ \qquad\qquad (\mu = 4.67) \\ + 2\mathrm{LiPCy_2} \xrightarrow{-\frac{1}{2}\mathrm{Ph_2}} \mathrm{Li_2CrPh_2(PCy_2)_2(THF)_4} \\ \qquad\qquad (\mu = 4.77) \end{cases} \qquad (2)$$

the second and third are in the $\mathrm{M_2CrR_4}$ class. Though paramagnetic, the latter two gave ^{1}H NMR spectra with phenyl signals at τ 2.72 and 2.75, respectively. No conclusions concerning the stability of the Cr(III) species, or, alternatively, the ease with which they are reduced to Cr(II), could be drawn.

Finally, there are the poorly characterized, polymeric $\mathrm{LiMnBu_3}$ and $\mathrm{LiMnEt_3}$ species.[31]

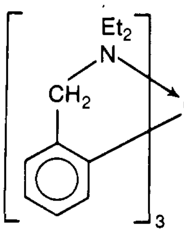
C. Cationic

No simple cationic complexes, $[\mathrm{MR}_x]^+$, have been reported, only cationic chromium complexes containing donor ligands, such as water (see section V.E) and amines. The latter are of the type *cis*-$[\mathrm{CrR_2(L\text{-}L)_2}]^+$ (R = Ph,[137,138] $\mathrm{CH_2SiMe_3}$,[139,140] anisyl,[138b,141,142] tolyl,[138b] and L-L = bpy, or R = Ph and L-L = phen.[137] It is also suspected that products with the composition $\mathrm{WMeCl_5L_3}$ (L = e.g., py) are ionic, i.e., $[\mathrm{WMeCl_4L_3}]^+\mathrm{Cl}^-$ (ref 143).

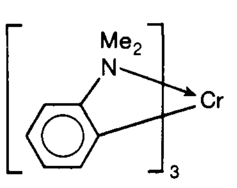
Orange-yellow $[\mathrm{CrPh_2(bpy)_2}]^+\mathrm{I}^-$ is slightly soluble in alcohol, THF, and acetone, and thermally stable (dec 230°). Salts containing other anions (X^- = Cl^-, Br^-, $\mathrm{NO_3}^-$, $\mathrm{ClO_4}^-$, $[\mathrm{BPh_4}]^-$ and $[\mathrm{BH_4}]^-$) may be prepared by reaction with AgX. Significant bond lengths from three crystal structures are shown in Table I. The results indicate little correlation between the Cr–C bond length and the compound's "stability".[140]

D. Chelating Alkyls and Aryls

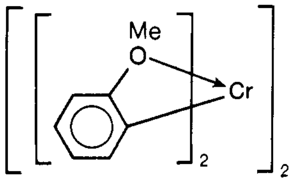
Several workers have prepared complexes containing alkyl or aryl ligands which chelate to the metal via a substituent donor. Their extraordinary thermal stability (the last decomposes at 350°) may be attributed to the fact that the ligands are sterically bulky, stereochemically rigid, and chelate strongly. Attempts to prepare Ti and V species containing the $\mathrm{C_5H_4NC_6H_4}$ ligand gave complexes which decomposed readily at room temperature.



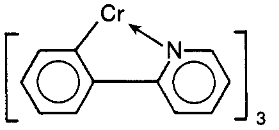
(ref 144)



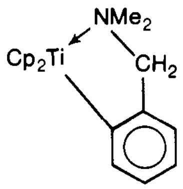
μ = 3.88
(ref 145)



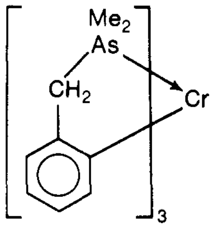
μ = 0.54
(ref 145)



μ = 3.64
(ref 146)



(ref 147)



μ = 3.80
(ref 148)

III. *Halide–Alkyl Complexes*

Halide–alkyl complexes, $\mathrm{MR}_y\mathrm{X}_z$ (X = halide), are usually prepared with a Grignard or lithium reagent deficiency or with milder alkylating agents like Zn, Hg, B, Al, Sn, or Pb alkyls. It is sometimes stated they are thermally less stable than binary alkyls, but the reverse in probably more often the case. They are best classified and discussed according to the metal.

A. Group 4

In 1959 Beermann and Bestian[149] reported the reaction of $\mathrm{TiCl_4}$ with $\mathrm{Me_2AlCl}$:

$$\mathrm{TiCl_4} + \mathrm{AlMe_2Cl} \xrightleftharpoons{\text{hexane}} \mathrm{TiMeCl_3} + \mathrm{AlMeCl_2}$$

Addition of excess NaCl effectively removed $\mathrm{AlMeCl_2}$ as $\mathrm{Na}^+[\mathrm{AlMeCl_3}]^-$. $\mathrm{TiMeCl_3}$ has also been prepared from reaction of $\mathrm{TiCl_4}$ with MeMgCl suspended in hexane[150] or with

$ZnMe_2$.[151] It also forms smoothly from any of the polymethylated Ti species and the appropriate quantity of $TiCl_4$.

Methyltitanium trichloride is a deep violet solid which is stable at room temperature and melts at 28–29° to give a *yellow* oil. It gives yellow solutions in saturated or aromatic hydrocarbons and is monomeric in benzene. Its red ether solutions probably contain $TiMeCl_3(ether)_x$. Surprisingly, $TiMeCl_3$ reportedly decomposes *more* rapidly in ether than in hydrocarbons, a reversal of the usual behavior for alkyls.[152] Decomposition in chlorinated solvents gives methyl chloride, in deuterated hydrocarbons only CH_4.[153]

Black-violet $TiMeBr_3$ was prepared by the $ZnMe_2$ route[151,152] and has properties analogous to $TiMeCl_3$. It has also been prepared admixed with $TiMe_2Br_2$ from $TiBr_4$ and MeMgBr suspended in benzene at 0–10° (ref 150). It is less stable than the trichloride, an observation which appears general for many halide–alkyl complexes.

Further alkylation of $TiMeCl_3$ with $AlMe_3$[149] or $ZnMe_2$[151] gives black $TiMe_2Cl_2$. It is markedly less stable than $TiMeCl_3$ and decomposes at ca. −10° to $TiCl_2$. Addition of dioxane to a yellow hexane solution gives a yellow dioxane adduct. ^1H NMR studies of methyl exchange between $ZnMe_2$ and $TiMe_2Cl_2$ and between $Ti(CD_3)Cl_3$ and $TiMe_2Cl_2$ have been described,[154] but the system's complexity makes interpretation difficult.

Berthold and Groh[18] briefly mentioned $TiMe_3I$, but no further details have appeared.

The $TiMe_nX_{4-n}$ (n = 1, 2, 3, 4) system is the only one in which at least one representative species has been isolated for each value of n. Thermal stability of the pure (solvent-free) complexes decreases in the order $n = 1 > 2 > 3 > 4$ and $X = Cl > Br > I$. More information on their solid-state structure could shed some light on the relationship of thermal stability to molecular structure. For example, $TiMeCl_3$ may be dimeric in the solid state as evidenced by its deep violet color, though it is monomeric and yellow in benzene.

Characteristically, complexes containing alkyl groups other than methyl are markedly less stable. The $TiRCl_3$ species have been prepared where R = ethyl,[149,151] propyl,[151] isobutyl,[149] and pentyl[151] employing alkylaluminum or zinc reagents but are stable only at low temperatures. Only blue to blue-violet bipyridyl adducts, $TiRCl_3(bpy)$, were isolated in low yield.[151] Yet Bawn and Gladstone report[155] that $TiEtBr_3$ (and $TiMeCl_3$) can be prepared from PbR_4 and TiX_4 (R = Me or Et, X = Cl or Br) in heptane or toluene. Pure $TiEtCl_3$, a violet solid which melts to a red liquid at room temperature, was obtained in 40–50% yield by vacuum distillation. In the presence of lead compounds it decomposes readily to C_2H_6, C_2H_5Cl, and Ti(IV) species. The zinc route also gives $TiEtCl_3$, as well as $TiPrCl_3$ and $Ti(n\text{-}C_5H_{11})Cl_3$.[152]

Phenyltitanium halides are prepared by arylation with diphenylzinc:[151,152]

$$TiX_4 + 0.5ZnPh_2 \xrightarrow[\text{pentane}]{-20°} TiPhX_3 + 0.5ZnX_2$$

$$(X = Cl, Br)$$

The reaction between $TiCl_4$ and LiPh in toluene at −50° also gives $TiPhCl_3$, but separation of lithium chloride is troublesome. Red-green dichroic $TiPhCl_3$ has properties analogous to $TiMeCl_3$ but is less thermally stable, suggesting that aryl complexes are not necessarily more stable than the corresponding alkyls, especially if the alkyl has no β hydrogen.

Several zirconium(IV) species can be prepared employing zinc reagents.[152,156] In contrast to the titanium system, zinc dialkyls (R = Me, Et, Pr) do not react with ZrX_4 (X = Cl, Br) in hexane. In ether they do, but only to give nearly insoluble solids containing zinc. However, in toluene at −10 to 0° brick-red solutions of $ZrMeX_3$ (X = Cl, Br) result. Addition of diethyl ether gives stable, isolable diethyl etherates, $ZrMeX_3(ether)_2$. In pyridine at 0° alkylation proceeds further to give brown solutions which probably contain the adducts, $ZnR_2X_2(py)_2$. These could not be isolated but addition of bipyridyl gave isolable $ZrR_2X_2(bpy)$. In no solvent did ZrX_4 react with SnR_4, consistent with the finding that $TiMeCl_3$ and $SnCl_4$ give $TiCl_4$ and $0.25SnMe_4$. Though $ZrR_2X_2(bpy)$, which is soluble in tetrahydrofuran and pyridine, is believed to be monomeric, the authors suggested $ZrRX_3(ether)_2$ is not, since it is only slightly soluble in ether. The authors also argue that ligand free alkyl complexes are more likely to be dimeric for zirconium than titanium.

What is believed to be $ZrPhCl_3(THF)_3$ has been prepared from PhMgCl and $ZrCl_4$ in toluene–THF.[157] Several adducts were isolated but extreme sensitivity to water and oxygen and low solubility made characterization difficult.

Titanium and zirconium benzyl complexes have been prepared[65] from $M(CH_2Ph)_4$ in toluene at −10° (eq 3). All are

$$\begin{tikzcd}
M(CH_2Ph)_4 + HX \arrow[r] \arrow[d, "MX_4"'] \arrow[dr, "BF_3"] & M(CH_2Ph)_3X \\
M(CH_2Ph)_2X_2 & Ti(CH_2Ph)_3F
\end{tikzcd} \qquad (3)$$

$$M = Ti;\ X = Cl, Br, I$$
$$M = Zr;\ X = Cl$$

rather unstable in solution and monomeric in benzene with the exception of $Ti(CH_2Ph)_3F$ whose apparent molecular weight is concentration dependent.

Partial alkylation of Ti(III) has been less successful. Treatment of $TiCl_3(THF)_3$ with 2 mol of LiPh in ether at −50° gives red-violet $TiPh_2Cl(ether)_3$ solutions.[27] Red crystals were isolated at temperatures below −50°. In pyridine an essentially identical procedure gives isolable, deep blue $TiRCl_2(py)_3$ species (R = Me or Ph) which are "fairly stable" at room temperature under nitrogen.[158] Kühlein and Clauss[159] prepared $TiMeCl_2$ at −78° in aliphatic hydrocarbons by a less direct approach:

$$2TiMeCl_3 + Hg(SiMe_3)_2 \rightarrow Hg + 2TiMeCl_2 + 2SiMe_3Cl$$

Isolated adducts are listed in Table II. Six-coordinate species are by far the most common. Five-coordinate species probably form in solution with some monodentate ligands, but isolation is rarely possible. At low temperatures the ^1H NMR spectra of $TiMeCl_3(L\text{–}L')$ (L–L′ = a chelating ligand) suggest a static *mer* configuration;[160] if the two ends of L–L′ are different, the preferred donor trans to Me is O > N > S.[161] In general the finding that TiR_4L_2 stability varies according to how firmly L is bound also holds true for $MR_nX_{4-n}L_2$ (M = Ti or Zr).

B. Group 5

The best known alkyl complexes of the vanadium triad are niobium and tantalum methyl complexes. In 1964 Juvinall[163] reported the low-yield preparation of $NbMe_3Cl_2$ and $TaMe_3Cl_2$ by alkylation with dimethylzinc in pentane. The volatile yellow complexes were trapped at −36° during solvent removal. Actually the reactions are quite clean and the products easily isolable.[164,165] Two are obtained virtually pure in high yield:

$$NbCl_5 + ZnMe_2 \xrightarrow[24\ h]{\text{pentane}} ZnCl_2 + NbMe_2Cl_3$$

$$TaCl_5 + 1.5ZnMe_2 \xrightarrow[1\ h]{\text{pentane}} 1.5ZnCl_2 + TaMe_3Cl_2$$

Traces of $NbMeCl_4$ or $TaMe_2Cl_3$ respectively can be converted to the more highly methylated complexes by addition of

TABLE II. Halide–Alkyl Adducts of the Group 4 Metals

M	R	X	L_n	Ref
Ti	Me	Cl_3	2CH_3CN, 2py, 2THF, 2Me_2S, 2THF, 2(1,4-thioxane)	162
			dme, 2,5-dithiahexane, dppe	160, 162
			bpy	151, 162
			TMEDA, *o*-$(Me_2N)_2C_6H_4$, *o*-$C_6H_4(OCH_3)(NMe_2)$	160
			$CH_3OCH_2CH_2NMe_2$, $CH_3OCH_2CH_2SMe$, $CH_3SCH_2CH_2NMe_2$, *o*-$C_6H_4(CH_2NMe_2)(NMe_2)$	161a
			THF, α-picoline, 1,4-dithiane	162
			Dioxane, PPh_3	149, 162
			$CH_3OCH_2CH_2CH{=}CH_2$	161b
Ti	Et, Pr, pentyl	Cl_3	bpy	151
Ti	Ph	Cl_3	2ether, 2py, bpy	151
Zr	Me_2	Cl_2,Br_2	bpy	156
Zr	Et_2	Cl_2, Br_2	bpy	156
Zr	Me	Cl_3, Br_3	2ether	156

TABLE III. Physical Characteristics and Spectroscopic Data for MMe_nCl_{5-n} (M = Nb or Ta, n = 1, 2, 3)

Complex	Color	Decompn[a]	Mol wt (found)[b]	Mass spec	^1H NMR (τ)[c]
$NbMeCl_4$	Orange-brown	65°	440[166]	$NbMeCl_4^+$[166]	6.65 (CH_2Cl_2, 34°)[95,164] 8.02 (CH_2Cl_2, −35°)[166] 7.52 (tol-d_8, −35°)[95]
$NbMe_2Cl_3$	Orange	RT, slowly	241[95]		7.10 (CH_2Cl_2, 34°)[95,164] 7.73 (tol-d_8, −35°)[95]
$NbMe_3Cl_2$	Yellow	RT, slowly		$NbMe_2Cl_2^+$[162]	7.40 (CH_2Cl_2, 34°)[164] 10.50 (CCl_4, −10°)[163] 7.75 (tol-d_8, −35°)[95]
$TaMeCl_4$	Yellow	Near 50°			7.22 (CH_2Cl_2)[95,164] 7.1 (CH_2Cl_2, −35°)[166] 7.92 (C_6D_6)[95]
$TaMe_2Cl_3$	Not isolated	RT, slowly	—		7.81 (CH_2Cl_2)[95,164] 8.32 (C_6D_6)[95]
$TaMe_3Cl_2$	Very pale yellow	RT, slowly	307[95]		8.23 (CH_2Cl_2)[95,164] 8.47 (C_6D_6)[95]

[a] RT = room temperature. [b] In benzene. [c] Some slight shifts occur upon lowering the temperature. All Nb species exhibit broad peaks at room temperature which sharpen on cooling. This behavior is more likely due to the onset of coupling to the ^{93}Nb nucleus (S = 9/2, 100% abundant) at higher temperature rather than to an exchange phenomenon.

the appropriate quantity of $ZnMe_2$ while $NbMe_3Cl_2$ may similarly be prepared quantitatively from $NbMe_2Cl_3$ (ref 95). Alkylation does not proceed beyond the trimethyl stage with $ZnMe_2$ though methyl group exchange between $NbMe_3Cl_2$ and $ZnMe_2$ in CCl_4 is rapid on the NMR time scale.[163] Monomethyl species form in about 95% purity in situ in aromatic hydrocarbons from either the di- or trimethyl species and the appropriate quantity of MCl_5. Since MCl_5 is nearly insoluble in pentane, $MMeCl_4$ cannot form completely.[164,165] Both $NbMeCl_4$ and $TaMeCl_4$ recently have been prepared and isolated from MCl_5 and 0.5$HgMe_2$ or 1.0$SnMe_4$ in CH_2Cl_2 at −35° (ref 166). Similar reactions with $NbBr_5$ were slower, required more alkylating agent, and gave markedly less stable $NbMeBr_4$ with difficulty. [Similarly, $TaMe_3Br_2$ (from $TaBr_5$ and $ZnMe_2$) decomposes slowly in the solid state at −35° to yield explosive, shock- or temperature-sensitive products.[95]] Finally, $TaMe_2Cl_3$ has only been prepared admixed with $TaMeCl_4$ and/or $TaMe_3Cl_2$. The compounds are listed in Table III (MR_4Cl species are unknown). The more volatile di- and trimethyl complexes are probably monomeric while the $MMeCl_4$ species are nearly dimeric in benzene.

A large number of adducts have been prepared with group 5 and 6 donor ligands.[164-167] Three types have been isolated: dimers containing a bridging ligand, e.g., $(NbMeCl_4)_2$(diox); normal six-coordinate species, e.g., $NbMe_2Cl_3(PPh_3)$; and seven-coordinate species containing a chelating ligand, e.g., $TaMe_3Cl_2$(bpy). The six-coordinate species are assumed octahedral. A crystal structure[168] of $TaMe_3Cl_2$(bpy) reveals a distorted capped trigonal prism with two of the methyl-metal bond distances equal to 2.24 and 2.16 Å. The third methyl and a chloride are disordered. Solution studies were hampered by redistribution reactions to give adducts of other MMe_nCl_{5-n} species and a tendency to dissociate a chloride ion as evidenced by conductivity measurements in dichloromethane. Attempted adduct formation with tertiary amines gave metal reduction (common for early transition metals) while oxygen was slowly abstracted from triphenylphosphine oxide, trimethylphosphine oxide, or $(Me_2N)_3P{=}O$.[166] Abstraction from the very stable P^V oxides illustrates niobium and tantalum's high oxygen affinity.

Several derivatives of $TaMe_3Cl_2$ [$TaCp_2Me_3$,[95] $TaMe_3(BH_4)_2$,[95] $TaMe_3(C_8H_8)$ (see section V.D.), $TaMe_3(BH_2(pz)_2)_2$,[169a] and $TaMe_3(acac)_2$[169a]] have been prepared straightforwardly.

Vanadium methyl and ethyl complexes have been mentioned briefly. Reaction of BMe_3 with VCl_4 yields VMe_2Cl_2 and $VMeCl_3$; with BEt_3, VEt_2Cl_2 results.[170] VR_2Cl_2 (R = Me, Et) may also be prepared employing ZnR_2 and several adducts are known.[152] Surprisingly, bright violet VMe_2Cl_2 reportedly does not dissolve in aliphatic hydrocarbons and decomposes at 150–170°.

The only other group 5 complexes are $Ta(CH_2CMe_3)_3Cl_2$,[84] $M(CH_2SiMe_3)_3Cl_2$ (M = Nb,[169b] Ta,[169c]), $M(CH_2SiMe_3)_2Cl_3$ (M = Nb or Ta),[169b,c] and $Ta(CH_2SiMe_3)Cl_4$.[169c] The first is formed from $TaCl_5$ and 3Me_3CCH_2MgCl in ether[84] or 1.5$Zn(CH_2CMe_3)_2$ in pentane.[95] The latter were prepared in ether from MCl_5 and $Zn(CH_2SiMe_3)_2$. All are thermally stable and most sublime in vacuo without decomposition at ca.

100°. Several recent attempts to prepare Nb and Ta benzyl complexes were reportedly unsuccessful.[72b]

C. Group 6

Phenylchromium halides have received greatest attention in group 6.

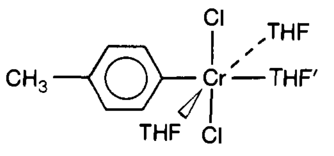
A series of $CrRCl_2(THF)_3$ complexes has been prepared employing organoaluminum compounds in THF:[171]

$$CrCl_3(THF)_3 + AlR_3 \text{ (or } AlR_2OEt) \xrightarrow{THF} CrRCl_2(THF)_3 + \text{traces of } CrCl_2(THF)_{1 \text{ or } 2}$$

$$R = Me, Et, Pr, \text{or } Bu^i$$

Yields can be high (79% for R = Et using $AlEt_2(OEt)$). Thermal stabilities decrease in the expected order (Me > Et > Pr > Bu^i), decomposition giving alkanes, alkenes, and alkyl coupling products. Decomposition of $CrMeCl_2(THF)_3$ in $CDCl_3$ (90°, 1 h) gave only traces of CH_3D. No evidence for chromium-hydrido species was found. Pyridine, acetonitrile, and bipyridyl adducts were also isolated.

Several of these compounds had been prepared earlier by other methods, for example, $CrMeCl_2(THF)_3$ from $CrCl_3$ and MeMgCl in THF.[172] A structure of one, Cr(*p*-tol)$Cl_2(THF)_3$,[173,174] reveals a *mer* geometry and an interesting Cr–O bond lengthening trans to the *p*-tolyl group. The authors suggested that a similar "trans effect" might be an important factor in the conversion of triarylchromium(III) compounds to bis(π-arene)chromium(0) or chromium(I) species; that is, loss of a trans ligand may be the initial step. Structural studies of $CrPh_2Cl(THF)_3$ (vide infra) and $CrPh_3(THF)_3$ would provide interesting comparisons.



Cr–C = 2.014 Å
Cr–O (THF) = 2.045 Å
Cr–Cl = 2.31 Å
Cr–O (THF′) = 2.214 Å

A benzyl complex, $Cr(CH_2Ph)Cl_2(THF)_3$, was believed to form at −20° in tetrahydrofuran[175] but only bibenzyl and $CrCl_2(THF)_2$ could be found after warming to 20°. Hydrolysis at low temperature gave $[Cr(CH_2Ph)(H_2O)_5]^{2+}$ (ref 176). A pyridine adduct was prepared by oxidation of $CrCl_2(py)_2$ with $PhCH_2Cl$:[176,177]

$$2CrCl_2(py)_2 + PhCH_2Cl \xrightarrow{py} CrCl_3(py)_3 + Cr(CH_2Ph)Cl_2py_3$$

Red-brown $Cr(CH_2Ph)Cl_2(py)_3$ decomposes at 40–60° in benzene or pyridine to give bibenzyl and Cr(II) salts, but the solid may be stored for months under dry nitrogen at 5–10°. It reacts with perchloric acid in water to give $[Cr(CH_2Ph)(H_2O)_5]^{2+}$ and with 1,3-cyclohexadiene to give benzene, toluene, and bibenzyl. Both $Cr(CH_2Ph)_2Cl(THF)_x$ and $Cr(CH_2Ph)_3(THF)_x$ are unstable in tetrahydrofuran.[175]

Steric factors must be responsible for coordination of only two THF molecules in $Cr(CHPh_2)Cl_2(THF)_2$:[50,178]

$$CrCl_3 + Ph_2CHLi(diox)_2 \xrightarrow[-50°]{THF} Cr(CHPh_2)Cl_2(THF)_2$$

The bright blue complex has a stability comparable to $CrMeCl_2(THF)_3$. Decomposition in THF–hexane, benzene, or ether gives $CrCl_2(THF)_2$ and $Ph_2CHCHPh_2$; $CrCl_2$(donor) forms in the presence of bpy, 2py, or dme (=donor). Complexes having only one halide, or none, could not be isolated.

Only one example of a CrR_2Cl species is reported. A redistribution reaction between $[CrPh_6]^{3-}$ or $[CrPh_5]^{2-}$ and $CrCl_3(THF)_3$ in dme gives $CrPh_2Cl(dme)_{1.5}$.[179] This completes the Cr(III) series, $CrPhCl_2$ to $[CrPh_6]^{3-}$ (solvents omitted).

Alkylation of WCl_6 with a variety of alkylating agents gives green, thermally unstable $WRCl_5$.[143,152,180a,181]

$$WCl_6 + 0.5MMe_2 \xrightarrow{-35°} WMeCl_5 + 0.5MCl_2$$

$$[M = Zn \text{ (in ether) or } Hg \text{ (in } CH_2Cl_2)]$$

$$WCl_6 + 0.5ZnPh_2 \xrightarrow[\text{room T}]{\text{ether}} WPhCl_5 \text{ (incomplete)}$$

$$WCl_6 + SnR_4 \xrightarrow{\text{hexane}} WRCl_5 + SnR_3Cl$$

$$(R = Me, Et, Bu, \text{or } Ph)$$

$$WCl_6 + \tfrac{1}{3}BR_3 \xrightarrow{\text{ether}} WRCl_5 + \tfrac{1}{3}BCl_3$$

$$(R = Me, Et, Bu)$$

Traces of Zn, Sn, or B possibly affect stability; i.e., one report[143] claims $WMeCl_5$ decomposes at −15°, another[181] at 65°. Authors noted that (i) WCl_6 and ZnR_2 (R = Et or Bu) in ether at −60° give WCl_4 which may be isolated as WCl_4L_2 (L = THF or py); (ii) WCl_6 and SnR_4 do not react in ether; and (iii) WCl_6 and ZnR_2 do not react in hexane. $WPhCl_5$ is apparently not well characterized. A recent report[180b] claims that diamagnetic $WPhCl_3$ (fine brown crystals) is the only pure product:

$$WCl_6 + 2SnPh_4 \xrightarrow[\text{pentane}]{\text{refluxing}} WPhCl_3 + 2SnPh_3Cl + PhCl$$

Some adducts, $WMeCl_5(py)_2$, $WMeCl_5(bpy)$, and $WEtCl_5(bpy)$, appear to be eight-coordinate while conductivity measurements suggest $WMeCl_5L_3$ (L = $NHEt_2$ and py) is ionic, i.e., $[WMeCl_4L_3]^+Cl^-$.

Extension of these studies to molybdenum was unsuccessful.[182] No Mo(V) species were isolated employing $MoCl_5$ and $ZnMe_2$, $SnMe_4$, or $ZnEt_2$ in hexane, ether, tetrahydrofuran, or pyridine. In ether, $MoCl_4$ and $0.5ZnMe_2$ gave $MoMeCl_3(ether)_2$ (insoluble, μ = 2.0) but in tetrahydrofuran or pyridine only $MoCl_3L_3$ (L = THF or py). Methane and methyl chloride were commonly observed products. Reaction of $MoCl_5$ and $AlPh_3$ gave similar results.[183]

D. Anionic Complexes

Anionic (or cationic) complexes should be isolable. Simple halide addition to niobium[165] and titanium[184,185] gives anions:

$$NEt_4Cl + NbMe_2Cl_3 \xrightarrow{CH_3CN} [NEt_4]^+[NbMe_2Cl_4]^-$$

$$NEt_4X + TiMeX_3 \xrightarrow{CH_2Cl_2} [NEt_4]^+[Ti_2Me_2X_7]^- \text{ (purple)}$$

$$[NEt_4]^+_2[Ti_2Me_2X_8]^{2-} \text{ (brown)}$$

$$\text{or} \quad [NEt_4]^+_2[TiMeX_5]^{2-} \text{ (blue)}$$

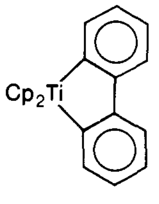
The dimers are believed analogous to $[Ti_2Cl_9]^-$ and $[Ti_2Cl_{10}]^{2-}$ which have (respectively) doubly and triply bridging chlorides. Interestingly, they are stable at room temperature only a short time while the mononuclear Ti anion is indefinitely stable. The latter is also stable toward oxygen. Reexamination of systems in which only neutral species were sought could be fruitful. For example, VMe_2Cl_2 and $ZnMe_2$ give $Zn[VMe_4Cl_2]\cdot OEt_2$ and LiMe and VCl_4 give $Li_2[VMe_4Cl_2]$.[152]

IV. Cyclopentadienyl-Alkyl Complexes

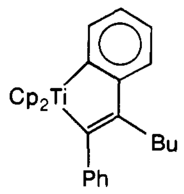
It is now believed that cyclopentadienyl "stabilizes" the metal-alkyl bond simply by occupying coordination sites which would otherwise be utilized in decomposition just as amines and phosphines promote stability by adduct formation. Readily available early metal cyclopentadienyl complexes have long been used to prepare many exemplary alkyl complexes.

A. Groups 4 and 5

Two groups prepared $TiCp_2R_2$ (R = Me, Ph, *m*-tolyl, and *p*-dimethylaminophenyl) approximately 20 years ago.[186-188] Other members of this class are $ZrCp_2Me_2$,[189a,195c] $HfCp_2Me_2$,[195c] MCp_2Ph_2 (M = Zr or Hf),[195c] $MCp_2(CH_2Ph)_2$ (M = Ti, Zr),[190-192] and $MCp_2(CH_2SiMe_3)_2$ (M = Ti, Zr, Hf).[86,87,89,193,194] The related π-indenyl species, $M(Ind)_2R_2$ (M = Ti, Zr, Hf, R = Me; M = Ti, Zr, R = Ph) have also been prepared.[195c] Several in which R_2 is a chelate are also known:



(ref 195a)



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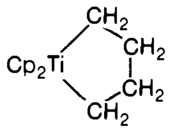
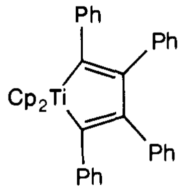


(ref 196)



(ref 197)

All were prepared from MCp_2Cl_2 and a lithium or Grignard reagent. Photolysis of MCp_2Me_2 (M = Ti, Zr, Hf) in the presence of $PhC\equiv CPh$ also reportedly gives $MCp_2(C_4Ph_4)$.[195b] Thermal stabilities are variable, approximately R = Me < CH_2Ph < Ph < CH_2SiMe_3 < chelates and Ti < Zr. For example, orange-yellow $TiCp_2Me_2$ blackens in the solid state at 40° and decomposes at ca. 0° in solution, while colorless $ZrCp_2Me_2$ sublimes with little decomposition at 100°. An exception is $TiCp_2(C_4H_8)$ which must be prepared and purified below −30°. In this case a carbon-carbon bond can cleave to yield $TiCp_2(C_2H_4)_2$, but β-hydrogen abstraction probably predominates. Interestingly, $Ti(\eta^5\text{-}C_5Me_5)_2Me_2$ is relatively stable,[198] suggesting that a bimolecular reaction or one involving hydrogen abstraction from the π-C_5H_5 ring may be one pathway by which MCp_2R_2 species decompose. Decomposition of several $TiCp_2R_2$ species (R = aryl or benzyl) has been studied recently.[199a] The structure of $TiCp_2Ph_2$ is pseudo-tetrahedral with a mean Ti–C bond length of 2.272 Å.[199b]

Several MCp_2RX (M = Ti or Zr, X = a halide) complexes are also known. Yellow $ZrCp_2MeCl$ was prepared from $(ZrCp_2Cl)_2O$ and trimethylaluminum[200] and in the following manner:[189a]

$$4ZrCp_2Me_2 + 2PbCl_2 \rightarrow 4ZrCp_2Me(Cl) + Pb + PbMe_4$$

The corresponding ethyl complex, $ZrCp_2(Et)Cl$, is reportedly stable only at 0° (ref 201). Those with R = cyclohexyl, 4-vinylbiphenyl, and 2-methyl-2-butyl are also only marginally stable;[189b] the carbon to which the metal is attached in the last two is uncertain.

$$ZrCp_2Cl_2 \xrightarrow[CH_2Cl_2,\ 0^\circ]{AlEt_3} ZrCp_2(Et)Cl\ (27\%)$$

Addition of 1 mol of RMgX to $TiCp_2Cl_2$ (R = Me, Et, Pr, Bu, Bu^i, *n*-C_5H_{11}, CH_2CMe_3, Ph, CH_2Ph, and CH_2CH_2Ph,[202] and CH_2SiMe_3[87]) gives the corresponding $TiCp_2RCl$ complexes. Their thermal stability appears greater than that for MCp_2R_2. Interestingly, $TiCp_2RCl$ apparently ionizes, even in nonpolar solvents, if R is CH_2CMe_3, Ph, or CH_2Ph, to give $[TiCp_2S_xR]^+$ (S = solvent). In acetonitrile treatment with $AgNO_3$ gave AgCl, but no organometallic products could be isolated.

Compounds containing one cyclopentadienyl ring, $TiCpMe_3$,[194,203] $TiCp(CH_2SiMe_3)_3$,[194,204] and $TiCpPh_3$,[205] are known. As might be expected, they are somewhat less stable than the corresponding $TiCp_2R_2$ species. $TiCpPh_3$ decomposes readily in ether to give biphenyl and $TiCpPh(ether)_2$ and gives $TiCpPh(NH_3)_2$ with NH_3.

Titanium(III) compounds, $TiCp_2R$, are obtained from $TiCp_2Cl$ and RMgX in ether (X = Cl or Br; R = Ph, *o*-, *m*-, and *p*-tolyl, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, or CH_2Ph).[206] The green, monomeric complexes have a magnetic moment close to the spin-only value for one unpaired electron (1.58 for R = Ph and 1.66 for R = 2,6-xylyl). Their thermal stabilities vary in the order R = *p*-tolyl ~ *m*-tolyl < Ph < CH_2Ph < *o*-tolyl < 2,6-xylyl ~ mesityl.[207] Attempts to prepare alkyl derivatives with R = Me, Et, Pr^i, or CMe_3 were unsuccessful though evidence for $TiCp_2Me$ by electrolytic reduction[208a] or on reaction of $TiCp_2Cl$ with MeMgX[208b] exists. $TiCp_2(CH_2SiMe_3)$[204] and $TiCp_2[CH(SiMe_3)_2]$[101a] are also known. The aryl complexes react with molecular nitrogen to give deep blue diamagnetic $(TiCp_2R)_2N_2$,[209] but $TiCp_2(CH_2SiMe_3)$ does not.

Only the analogous vanadium(III) complexes (R = Ph,[210,211] Me,[212] or CH_2Ph[212]) were isolated starting with VCp_2Cl_2 or VCp_2Cl. That steric factors do not allow VCp_2R to form is suggested by the following: (1) $VCp_2(C\equiv CPh)_2$ can be prepared, presumably since the alkynyl ligand has minimal steric requirements; (2) the allyl ligand in $VCp_2(C_3H_5)$ is σ-bonded, not π-bonded as in the corresponding titanium and niobium complexes; and (3) the nitrogen ligand in $VCp_2(o\text{-}Me_2NCH_2C_6H_4)$ is not coordinated as in the corresponding Ti complex.[147] Interestingly, while VCp_2R (R = Me or CH_2Ph) reacts with CO to give $VCp_2(CO)(COR)$, VCp_2Ph yields $VCp(C_5H_5Ph)(CO)_2$[213] (cf. Ph migration to C_8H_8, section V.D, and Et to η^5-C_5H_5[214]).

ESR evidence suggests that addition of a large excess of RMgX (R = Et, Me, Pr^i) to $TiCp_2Cl$ gives $[TiCp_2R_2]^-$ (ref 208b). Surprisingly, not only $[TiCp_2Me_2]^-$, but $[TiCp_2Et_2]^-$ was proposed to be stable for 1–2 h at room temperature in THF under the experimental conditions employed.

The only known $TiCpRR'$ species are the following:[79,215]

$$TiCp_2Ph_2 + LiCH_2Ph \rightarrow TiCpPh(CH_2Ph)$$

$$TiCp_2(CH_2Ph)_2 + LiCH_2Ph \rightarrow TiCp(CH_2Ph)_2$$

Addition of LiPh to $TiCp_2Ph_2$ reportedly[187] gives $[TiCp_2Ph_3]^-$, which decomposes[216] via intermediate $TiCpPh_2$.

Paramagnetic $NbCp_2R_2$ (R = Ph,[217,218] Me,[219] and CH_2SiMe_3[86]) and $TaCp_2Me_2$[219] are more stable than diamagnetic $TiCp_2R_2$, suggesting that an unpaired electron (if this were the only criterion) does not markedly decrease stability. At −45° $NbCp_2Ph_2$ reacts normally with HCl in ether to give $NbCp_2Cl_2$ and 2 mol of benzene, but, curiously, neither product is found when the reaction is carried out at room temperature.[218]

Finally, two rather unusual compounds with the MCp_2 basic unit are known. The first is $ZrCp_2(H)Me$[220] which was prepared from $ZrCp_2MeCl$ and $LiAlH_4$ or $LiAl(OCMe_3)_3H$ in tetrahydrofuran. Its insolubility in common organic solvents

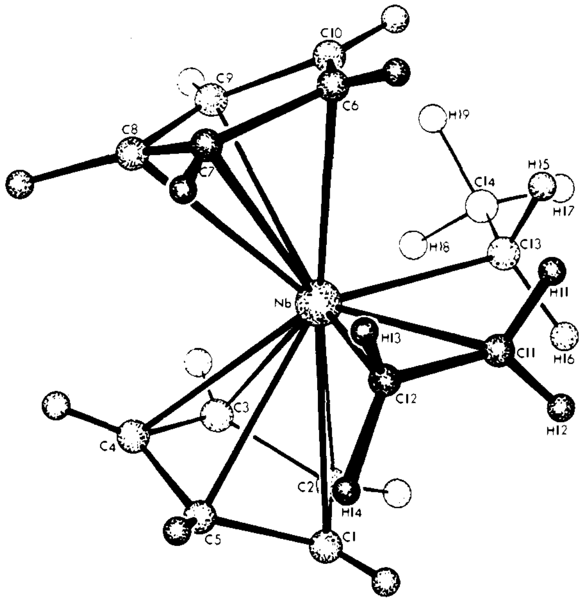


Figure 8. The structure of $Nb(\eta^5\text{-}C_5H_5)_2(C_2H_4)(C_2H_5)$.

and broad ν_{M-H} infrared band at low frequencies (1500, 1310; ν_{M-D} = 1090, 965) suggest a polymeric structure which presumably does not allow reductive elimination to give methane and $ZrCp_2$. The second is $NbCp_2Et(C_2H_4)$:[221]

$$NbCp_2H_3 \xrightarrow[-H_2]{C_2H_4} NbCp_2(H)(C_2H_4) \underset{-C_2H_4}{\overset{C_2H_4}{\rightleftharpoons}} NbCp_2Et(C_2H_4)$$

The crystal structure[222] shows that the Et and C_2H_4 carbon atoms all lie in a plane which passes through Nb and bisects the Cp–Nb–Cp angle (Figure 8). On loss of ethylene β-hydrogen abstraction regenerates $NbCp_2(H)(C_2H_4)$.

B. Groups 6 and 7

Many $MCp(CO)_3R$ (M = Cr, Mo, or W), $CrCp(NO)_2R$, and $MoCp_2(NO)R$ complexes have been prepared, most often by the salt method;[223] for example

$$0.5[MoCp(CO)_3]_2 \xrightarrow{Na/Hg} Na^+[MoCp(CO)_3]^- \xrightarrow{RX} MoCp(CO)_3R$$

Exotic preparative schemes have also been used

$$MoCp(CO)_3H + CH_2N_2 \rightarrow MoCp(CO)_3Me \quad \text{(ref 188)}$$

$$[ReCp(CO)_2(NO)]^+ + NaBH_4 \rightarrow ReCp(CO)(NO)Me \quad \text{(ref 224)}$$

as well as straightforward methods

$$CrCp(NO)_2I + MeMgI \rightarrow CpCr(NO)_2Me \quad \text{(ref 188)}$$

Variations in R and other ligands (for example, tripyrazolylborate[225] for Cp or tertiary phosphines for CO) are many, and a full discussion of their preparation and chemistry is not possible in this article [see ref 226–228 and earlier reviews].

The system based on MCp_2Cl_2 (M = Mo or W) has yielded many new species, the chemistry of which is developing rapidly:[214,229–231]

$$MoCp_2Cl_2 + AlCl_2Et \rightarrow MoCp_2ClEt$$

$$MCp_2(C_2H_3R) \xrightarrow{R'X} [MCp_2(C_2H_3R)R']^+$$

(M = Mo, R = H, R′ = Me; M = W, R = H, Me,

(R′ = Me or CH_2Ph; X = halide)

$$[MCp_2(H)(C_2H_3R)]^+ \xrightarrow{PPh_3} [MCp_2(PPh_3)(CH_2CH_2R)]^+$$

(R = H, M = Mo; R = Me, M = W)

$$WCp_2H_2 + C_6H_6 \xrightarrow[\text{isoprene}]{h\nu} WCp_2Ph(H)$$

$$WCp_2H_2 + \text{mesitylene} \xrightarrow{h\nu} WCp_2(CH_2C_6H_3Me_2)_2$$

$$[MoCp_2(C_2H_4)Me] \xrightarrow{PPhMe_2} [MoCp_2Me(PPhMe_2)]^+$$

$[MCp_2(\text{olefin})R]^+$ species almost certainly have a structure analogous to $NbCp_2Et(C_2H_4)$ (vide supra). The crystal structure[229c] of $WCp_2(CH_2\text{-}3,5\text{-}Me_2C_6H_3)_2$ reveals a M–C bond length of 2.28 and 2.29 Å and Cp–W–Cp angle of 75°. The authors propose that it and $WCp_2(CH_2\text{-}p\text{-}C_6H_4Me)_2$ form by insertion of W into a methyl C–H bond.

V. *Other Alkyl Complexes*

Since it is now believed that the transition metal to carbon bond is not inherently weak (see section VI.E), the role of other ligands in determining the stability and reactivity of a given complex will be examined more closely in the future. Several classes of complexes containing an alkyl or aryl ligand are discussed below according to the type of "ancillary" ligand.

A. Alkoxides

In 1952 Herman and Nelson reported[232–235] the first stable complex containing a carbon–titanium bond, $TiPh(OPr^i)_3$ (eq 4). It can be stored indefinitely in the dark at 10° but decomposes rapidly at its melting point (88–90°) to give biphenyl and, at ca. 200°, also a 1:1 mixture of saturated and unsaturated C_4 hydrocarbons. The stability of $TiPh(OPr^i)_3$ and analogous compounds was proposed to be primarily a function of the substituent groups' electronegativity. A stability order for TiR_nX_{4-n} complexes was suggested: R = Bu < Me < ethynyl < p-anisyl < Ph < α-naphthyl < indenyl; X = OPr^i ~ OPr ~ OBu ~ OBu^i > OMe ~ Cl > F; and n = 1 > 2 > 3 > 4. The structure of $TiPh(OPr^i)_3$ is unknown, but a dimeric formulation with two bridging alkoxide groups is plausible.

$$Ti(OPr^i)_4 + LiPh/LiBr \xrightarrow{\text{ether}}$$

$$TiPh(OPr^i)_3 \cdot LiOPr^i \cdot LiBr \cdot \text{ether} \xrightarrow{0.25TiCl_4} TiPh(OPr^i)_3 +$$

$$0.25Ti(OPr^i)_4 + LiCl + LiBr + \text{ether} \quad (4)$$

(53%)

The analogous methyl complex, a distillable (50°, 0.01 mm), viscous, yellow liquid is prepared from $Ti(OPr^i)_3Cl$ and LiMe in ether at −50° (ref 236, 237). Nonvolatile $TiMe(OEt)_3$ was prepared similarly. Addition of a second LiMe to $TiMe(OPr^i)_3$ gives $TiMe_2(OPr^i)_2$. Both the mono- and dimethyl compounds undergo redistribution reactions with $TiMeCl_3$:

$$2TiMe(OR)_3 + TiMeCl_3 \xrightarrow{CH_2Cl_2} 3TiMe(OR)_2Cl$$

85%

$$TiMe(OR)_3 + 2TiMeCl_3 \longrightarrow 3TiMe(OR)Cl_2$$

$\nearrow$ 80%

(also $TiCl_4 + TiMe_2(OR)_2$) (R = Pr^i or Et)

All may not be monomeric; for example, $TiMe(OPr^i)_2Cl$ is soluble in pentane, melts at 62–64°, and sublimes in vacuo, while $TiMe(OEt)Cl_2$ is only slightly soluble in toluene. The apparent molecular weight (362) of $TiMe(OPr^i)_3$ in benzene indicates some tendency to dimerize.

One member of the $TiR_n(OR')_{4-n}$ family, $Ti(CH_2Ph)_2(OEt)_2$, which is known to be dimeric in benzene,[65] decomposes least rapidly of the series $Ti(CH_2Ph)_3F > Ti(CH_2Ph)_3Cl > Ti(CH_2Ph)_2Br_2 > Ti(CH_2Ph)_3Br > Ti(CH_2Ph)_4 > Ti(CH_2Ph)_2(OEt)_2$. Generalization is difficult since $Ti(CH_2Ph)_3F$ is also strongly associated in benzene. An attempt to correlate structure with stability would be valuable but appears premature.

A titanium complex containing the chelating 2-methyl-2,4-pentanediolate ligand can be isolated in good yield:[238]

$$TiCl_2(C_6H_{12}O_2) + 2MeMgI/ether \xrightarrow[THF]{-10°} TiMe_2(C_6H_{12}O_2)$$

A dimeric structure was suggested by molecular weight and confirmed by x-ray studies.[239] Each titanium has a trigonal-bipyramidal geometry with two methyl groups located in the trigonal plane (Figure 9). The Ti-O(bridging) bond lengths are longer (1.97-2.06 Å) than the Ti-O(terminal) (1.77 and 1.78 Å), while the Ti-carbon distances vary from 2.11 to 2.19 Å. The compound decomposes slowly at room temperature in the solid state or in solution.

In addition to the direct method, alkoxides, in principle, may be prepared by reaction of metal alkyls with alcohol or oxygen (see section VII.C). Ether cleavage is more unusual:[37]

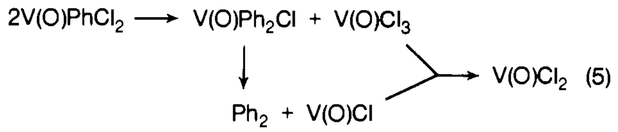
$$[ZrPh_2(ether)]_2 \xrightarrow{heat} 2ZrPh(OEt) + C_6H_6 + 0.5biphenyl + 0.5C_2H_6 + 1.5C_2H_4$$

Alkoxide ligands can take part in decomposition reactions, though most likely only under extreme conditions, for example, in the high temperature decomposition of $TiPh(OPr^i)_3$.[232]

B. Oxo

Allowing $VOCl_3$ to react with a deficiency of Grignard reagent or passing $V(CH_2SiMe_3)_4$ through a cellulose column gives lemon-yellow $V(O)(CH_2SiMe_3)_3$ which is relatively air stable, sublimes in vacuo (70°), and is light sensitive.[88] It does not react with water, alcohols, carbon monoxide, tertiary phosphines, or primary amines under mild conditions.

The reaction of $V(O)Cl_3$ with $HgPh_2$[240,241] or $ZnPh_2$,[240] but not $SnPh_4$, in aliphatic hydrocarbons at −25° gives red, crystalline $V(O)PhCl_2$. It is stable in hydrocarbons at <−25° but at ca. −10° gives biphenyl, chlorobenzene, and a trace of benzene in what is believed to be a concerted, *nonhomolytic* decomposition[241] (eq 5). With $Hg(C_6H_5D)_2$ (92.8% monodeuterated), dilabeled biphenyl results. Oxygen "insertion" into the metal-phenyl bond may occur since hydrolysis of the product prepared with 0.5 mol of $HgPh_2$ gives a 75% yield of phenol. Surprisingly, electron donors *destabilize* $V(O)PhCl_2$; in ether it decomposes completely in minutes at −50°. However, isolation of $V(O)PhCl_2(bpy)$ was successful (dec 14°). Reaction of $V(O)Cl_3$ with $SnMe_4$ did not occur, while $ZnMe_2$ gave a product from which $ZnCl_2$ could not be removed.[240]



$$2V(O)PhCl_2 \longrightarrow V(O)Ph_2Cl + V(O)Cl_3 \quad (5)$$
$$V(O)Ph_2Cl \longrightarrow Ph_2 + V(O)Cl; \quad V(O)Cl + V(O)Cl_3 \longrightarrow V(O)Cl_2$$

Reaction of $V(O)(OPr^i)_3$ with $HgPh_2$ failed to give $V(O)Ph(OPr^i)_2$ in either ether or benzene[242] but in pentane $ZnMe_2$ reacted smoothly:

$$V(O)(OPr^i)_3 + ZnMe_2 \xrightarrow{pentane} V(O)Me(OPr^i)_2 + ZnMe(OPr^i)$$

The red-brown viscous product can be distilled in vacuo (50°, <2 mm) but decomposes rapidly at 70°. No adducts (e.g., with bipyridyl) could be isolated. The parent ion was the highest peak in the mass spectrum.

Methylmagnesium iodide reduces $NbOCl_3$ to $NbOCl_2$ in ether but not in toluene-ether mixtures (ca. 2:1) at −15°.[243] Only $NbMeOCl_2$ adducts, e.g., $NbMeOCl_2(OPMe_3)_2$, which was also prepared from $NbMeCl_4$ and $3OPMe_3$, could be isolated. No reaction was observed between $NbOCl_3$ and $HgMe_2$ or $SnMe_4$ under a variety of experimental conditions.

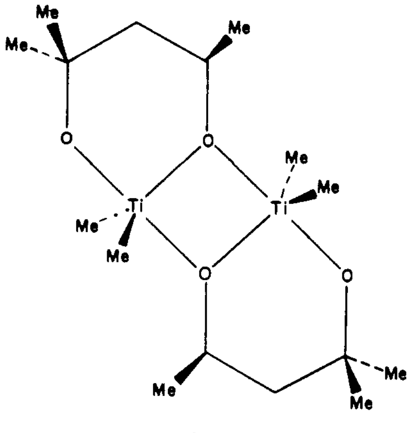


Figure 9. Schematic drawing of $[TiMe_2(C_6H_{12}O_2)]_2$.

The tungsten complexes, $WCp_2(O)R_2$ (R = Me, Et, Ph, or CH_2Ph), were prepared from WCp_2OCl_2 and RMgI in ether or tetrahydrofuran.[244] They decompose on attempted sublimation at ca. 60°. The phenyl and benzyl compounds are moderately stable in air.

At −78° in CH_2Cl_2, $W(O)Cl_4$ and $HgMe_2$ give $W(O)MeCl_3$.[181] It is markedly more unstable than $WMeCl_5$ and decomposes at ca. −10°. The HMPA adduct, $W(O)MeCl_3(HMPA)$, was also obtained from reaction of $WMeCl_5$ with HMPA.

Finally, $Re(O)(PPh_3)_2Cl_3$ or $Re(O)Cl_4$ reacts with methyllithium to give thermally stable, red-purple $Re(O)Me_4$ (mp 44°).[245] Its mass spectrum shows the parent ion and its infrared spectrum the characteristic strong Re═O stretch at 1016 cm^{-1}. Its ESR spectrum at −175° suggests a tetragonal-pyramidal structure. It is thermally stable in the vapor state to ca. 150° and does not react with water, alcohols, H_2, CO, or SO_2 under mild conditions. With I_2 it gives CH_3I quantitatively and both O_2 and NO react rapidly to give as yet uncharacterized products.

C. Dialkylamido

A series of complexes, $Ti(NR_2)_3(R')$ (R = Me, R′ = Me, CD_3, Et; R = Et, R′ = Me, CD_3, Pr, Pr^i, Bu, CMe_3 and Ph), were prepared from $Ti(NR_2)_3X$ and R′MgX or LiR′ (X = a halogen).[246] They all melt below room temperature, sublime easily in vacuo, and decompose around 70°. All were characterized unambiguously by ^1H NMR. Note that R′ can be isopropyl or even *tert*-butyl, ligands which are normally susceptible to β-hydrogen abstraction. The bulky NR_2 ligands apparently discourage both decomposition and adduct formation with typical donor ligands. Decomposition[247] gives methane and diamagnetic Ti(IV) residues:

$$Ti[NMe_2]_3(CD_3) \rightarrow 30\%\ CH_2D_2,\ 30\%\ CHD_3,\ 30\%\ CD_4 + Ti(IV)$$

$$Ti[NEt_2]_3(CD_3) \rightarrow 50\%\ CH_2D_2,\ 20\%\ CH_3D,\ 20\%\ CHD_3 + Ti(IV)$$

the authors proposed abstraction from the dialkylamido group by an "ionic" rather than radical mechanism.

D. Cyclooctatetraene

Complexes of the type $Zr(C_8H_8)R_2$ (R = Me, Et) have been prepared from $Zr(C_8H_8)Cl_2$.[248] The dimethyl derivative forms a yellow dietherate in which the ether may be bound to the metal. If C_8H_8 is planar, the adducts are monomeric, 18-electron species. The methyl compound decomposes to give methane and the ethyl to give 67% C_2H_6, 14% C_2H_4, and 10% of a mixture of butane and butenes (4.5:5.5 ratio) in 4 h at 60°.

Niobium and tantalum complexes containing both cyclooctatetraene and alkyls are also known:[249]

$$MCl_5 + \begin{matrix}1.\ 2[K^+]_2[C_8H_8]^{2-}\\ 2.\ LiR\end{matrix} \xrightarrow[-78°]{\text{toluene}} M(C_8H_8)_2R$$

(M = Nb or Ta, R = Me, or Ph)

$$MRCl_4 + 2[K^+]_2[C_8H_8]^{2-} \xrightarrow[-78°]{\text{toluene}} M(C_8H_8)_2R$$

(M = Nb, R = Me; M = Ta, R = Me or Ph)

$$TaMe_3Cl_2 + [K^+]_2[C_8H_8]^{2-} \xrightarrow[-78°]{\text{toluene}} Ta(C_8H_8)Me_3$$

The red-brown, crystalline $M(C_8H_8)_2R$ complexes are moderately soluble in tetrahydrofuran and dichloromethane and do not sublime without decomposition while $Ta(C_8H_8)Me_3$ is blue, sublimes nicely at 100° and 1 μ, and is soluble in aromatic hydrocarbons. In $M(C_8H_8)_2R$ one C_8H_8 ring is believed planar (η^8), the second diene-like (η^4). Monomeric $Ta(C_8H_8)Me_3$ most likely has a planar C_8H_8 ring with three methyl groups disposed in a tripod-like fashion. When $M(C_8H_8)_2Ph$ reacts with dmpe or diars, the Ph ligand migrates to a C_8H_8 ring to give complexes containing a 2,3,4,5,6-η-*endo*-8-phenylbicyclo[5.1.0]octadienyl ligand, $M(C_8H_8)(C_8H_8Ph)(L\text{–}L)$ (L–L = dmpe or diars).

E. Aquo

Benzyl chloride[250,251] or radicals generated from $PhCH_2CMe_2OOH$[252] oxidize $Cr(ClO_4)_2$ to give $[Cr(H_2O)_5(CH_2Ph)]^{2+}$ in aqueous solution. The former, in which benzyl radicals are postulated, resembles formation of $[Co(CH_2Ph)(CN)_5]^{3-}$ from benzyl bromide and $[Co(CN)_5]^{3-}$ (ref 253).

$$PhCH_2Cl + Cr^{2+} \rightarrow CrCl^{2+} + PhCH_2\cdot$$

$$PhCH_2\cdot + Cr^{2+} \rightarrow Cr(CH_2Ph)^{2+}$$

The analogous methyl complex was first postulated as a minor product of Cr^{2+} oxidation with Me_3COOH[254,255] but later was similarly prepared and isolated in perchloric acid by ion-exchange chromatography.[256] It may also be obtained by methyl group transfer from an organocobaloxime[257] or corrin[258] complex to aqueous Cr^{2+}:

$$CoR(Hdmg)_2(H_2O) + Cr^{2+} + 2H^+ \rightarrow Co^{2+} + [Cr(H_2O)_5(R)]^{2+} + 2H_2dmg$$

(dmg = dimethylglyoxime)

It is relatively stable ($t_{1/2}$ = several hours at 0°) in perchloric acid as are its Et and Pr analogs.

The striking fact, of course, is that the metal–carbon bond survives in an aquo complex and is cleaved only relatively slowly even in aqueous acid[259] (the rate is dependent on $[H^+]$). The fact that it is dicationic and/or that Cr(III) substitution processes are slow must account for its stability in aqueous acid.

F. Carbonyl

One of the few group 7 alkyl species, $M(CO)_5R$ [M = Mn, Re], is prepared by alkylation of $[M(CO)_5]^-$ (ref 223) or by decarbonylation of $RCOM(CO)_5$.[260] Like most "18-electron" monoalkyl complexes containing relatively nonlabile ligands, R can vary widely. They are probably best classed as carbonyls and will not be discussed here (see ref 226, 227, 261).

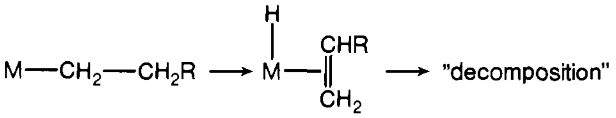
VI. Decomposition

Transition-metal alkyl decomposition modes have been discussed frequently and studied specifically for Ti,[19,20,262-268] V,[269,270] Cr,[270-275] and Mn,[32] in addition to metals outside groups 4–7 (see ref 276). However, no unified theory of decomposition, or even a clear understanding of specific cases (with one or two exceptions), has resulted. Wilkinson,[83] Baird,[276] Braterman and Cross,[277-279] and Mingos,[280] among others, discuss decomposition broadly. We intend to present what we feel are the most pertinent results which support postulated decomposition pathways. Much mechanistic information derives from studies of platinum alkyls, which are experimentally convenient because of stability to air, but the results probably apply equally well to early transition metal alkyls.

A. β-Hydrogen Abstraction

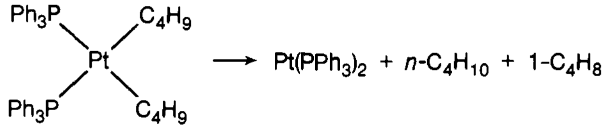
Recognition that many transition metal alkyl derivatives decompose by abstraction of a β-hydrogen atom has had substantial practical consequences. The number of isolable alkyl compounds is growing rapidly through use of alkyls lacking a β-hydrogen as described in preceding sections. The very success of this approach carries with it the danger that β-abstraction will be overemphasized.

β-Hydrogen abstraction or elimination can describe more than one reaction, the overall results of which may be identical. The best documented and the one usually meant by "β-hydrogen elimination" is intramolecular β-hydrogen abstraction by the metal:



$$M{-}CH_2{-}CH_2R \longrightarrow \overset{H}{\underset{}{M}}{-}\overset{CHR}{\underset{CH_2}{\|}} \longrightarrow \text{"decomposition"}$$

The best-studied example is $Pt(PPh_3)_2(n\text{-}C_4H_9)_2$:[281]



The following are pertinent:

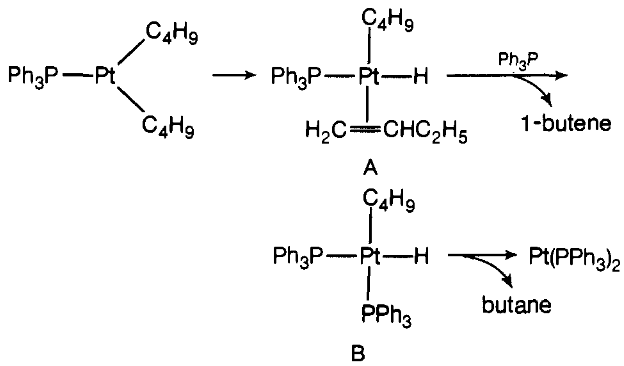
(1) Decomposition is a first-order intramolecular process.

(2) Addition of PPh_3 decreases the rate; presumably PPh_3 dissociation is inhibited.

(3) Deuterium in the 1,1-$C_4D_2H_7$ derivative is extensively scrambled in the 1-butene product.

(4) Added 1-butene does not exchange during the decomposition.

An important point is that β-hydrogen abstraction from polyalkyl complexes can give equal amounts of alkane and al-



kene, a phenomenon once thought characteristic of homolytic M-C bond cleavage. Butene presumably arises by β-abstraction to give A, from which it dissociates, while butane forms by reductive elimination (section VI.D) from the hydrido-butyl compound, B. Presumably these principles can be applied to many systems, though rarely can decomposition be ascribed to this specific mode, excluding all others.

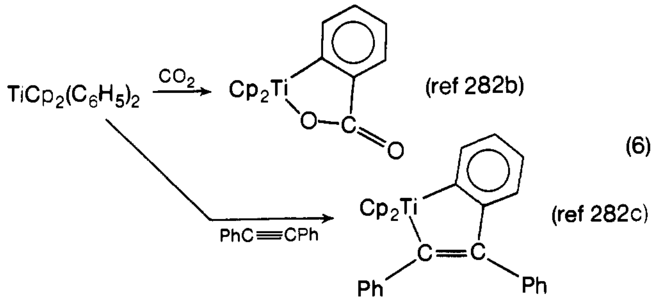
In the early transition metals, a nice example of β-hydrogen abstraction is the thermolysis of $\mathrm{NbCp_2Et(C_2H_4)}$ to give isolable $\mathrm{NbCp_2(C_2H_4)(H)}$.[221] With only a single alkyl group on the metal, alkane should not form unless an intermolecular reaction occurs:

$$\mathrm{M\text{-}H + M\text{-}R \rightarrow 2M + RH}$$

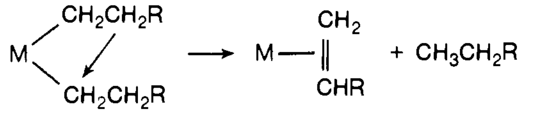
A β-hydrogen may also be abstracted from an aryl ligand. In $\mathrm{TiCp_2Ph_2}$ or its $\mathrm{C_6D_5}$ analog either Ti or phenyl abstracts an ortho hydrogen to give benzene[282a]

$$\mathrm{Cp_2Ti(C_6D_5)_2} \xrightarrow[24\ \mathrm{h}]{\mathrm{C_6H_6},\ 80^\circ} \mathrm{C_6D_6}\ (1\ \mathrm{mol})$$

Evidence for a phenylene complex, "$\mathrm{Cp_2Ti(C_6H_4)}$", consists of in situ reactions with $\mathrm{CO_2}$ or PhC≡CPh (eq 6). Phenylene complexes have also been postulated in Cr,[13] W, Nb, and Ta,[132b] and Mo[110b] systems.

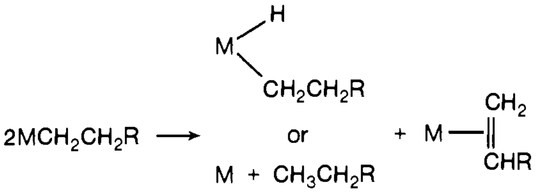


As mentioned above, a β hydrogen can be abstracted directly by another alkyl:



Of course, the overall result is identical with abstraction by the metal.

Finally, *inter*molecular abstractions of both types are possible (eq 7). Again they cannot be distinguished from each other, but in theory can be distinguished from intramolecular abstraction since the formal oxidation state of the metal is reduced by only one.



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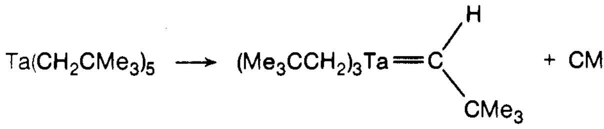
B. α-Hydrogen Abstraction

Much less well recognized is a process in which an α-hydrogen of an alkyl ligand is abstracted to give an alkylidene, or carbene, complex. A substantial amount of information indicates this is also a significant decomposition mode.

As for β-abstraction, α-abstraction can occur in four ways. Intramolecular abstraction by the metal has been suggested by several authors.[230,265,283-287] This process, $\mathrm{M\text{-}CHR_2 \rightarrow M(H)(CR_2)}$, is more likely to occur in complexes with less than 18 valence electrons since the number must increase by two; the relationship to formal metal oxidation state is less clear. What is perhaps the first evidence of *inter*molecular α-hydrogen abstraction, photolysis of $\mathrm{CD_3TiCl_3}$ in hydrocarbons to give $\mathrm{CD_4}$ and a series of perdeuterioalkanes up to $\mathrm{C_9D_{20}}$,[153] could involve a transient $\mathrm{CD_2{=}M}$ complex. However, photolysis of metal alkyls is, in general, even less well understood than thermolysis.

The only documented example is an apparent intramolecular α-abstraction by another alkyl[94] (eq 8 and 9). The neo-

$$\mathrm{Ta(CH_2CMe_3)_3Cl_2 + 2LiCH_2CMe_3 \longrightarrow \text{"}Ta(CH_2CMe_3)_5\text{"} + 2LiCl} \quad (8)$$

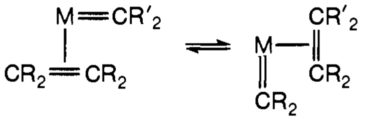


(9)

pentylidene ligand probably forms by abstraction of a neopentyl α-proton by a neighboring neopentyl group in the sterically crowded penta(neopentyl) intermediate. An analogous α-abstraction may occur in the thermal decomposition of $\mathrm{Ti(CH_2Ph)_4}$ in which 2.66 mol of toluene is generated per mole of complex,[65] exactly the amount predicted by redistribution of all α hydrogens to give toluene and "Ph C(Ti)$_3$".

The dimeric species, $\{\mathrm{M[CH_2SiMe_3]_2[CSiMe_3]}\}_2$ (M = Nb or Ta),[83,84] possibly form from incipient $\mathrm{M[CH_2SiMe_3]_3[CHSiMe_3]}$ by a second α-hydrogen abstraction from $\mathrm{CHSiMe_3}$ by $\mathrm{CH_2SiMe_3}$. Intermolecular reactions, possibly including the Grignard reagent, are also likely.[84] In a related vein, toluene is produced on addition of $\mathrm{Al(CH_2Ph)_3}$ to $\mathrm{Ti(CH_2Ph)_4}$.[65] Interestingly, however, *alkylidene* α hydrogens are possibly more easily abstracted as suggested by the reaction of $\mathrm{Ta(CH_2CMe_3)_3(CHCMe_3)}$ with $\mathrm{LiR{\cdot}L_x}$ to give $\mathrm{Ta(CH_2CMe_3)_3[C(CMe_3)(Li{\cdot}L_x)]}$.[94,96]

Carbenes may be formed in olefin disproportionation systems, possibly by α-hydrogen abstraction. Disproportionation via equilibrium 10 has been proposed.[286-289]



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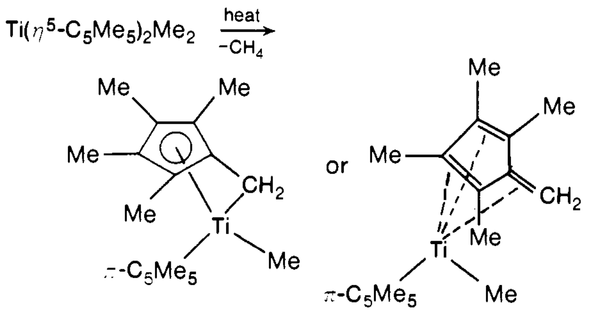
C. Ligand Hydrogen Abstraction

Several examples demonstrate that nonalkyl ligands donate hydrogen in a decomposition reaction in which alkane is produced. For example, $\mathrm{Ti(\eta^5\text{-}C_5Me_5)Me_2}$ decomposes as shown in eq 11.[198] Apparently α-abstraction to give $\mathrm{Ti(\eta^5\text{-}C_5Me_5)_2(CH_2)}$ and methane is unfavorable. Perhaps the cyclopentadienyl's methyl protons are more acidic than the metal's methyl protons. Similar examples are (i) H abstraction from $\eta^5\text{-}\mathrm{C_5H_5}$ in $\mathrm{UCp_3R}$ decomposition,[290] (ii) abstraction from the ethyl group of a diethylamido ligand in $\mathrm{Ti(NR_2)_3R'}$ species,[246] and (iii) abstraction of ortho hydrogen in a $\mathrm{PPh_3}$ ligand in $\mathrm{M(PPh_3)_3Me}$ (M = Rh[291] or Ir[292]) to give $\mathrm{M(C_6H_4PPh_2)(PPh_3)_2}$ and $\mathrm{CH_4}$ (see also ref 16a).



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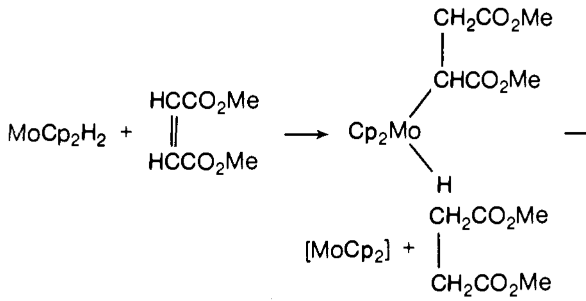
D. Reductive Elimination (Coupling)

Conceptually one of the simplest decomposition modes of a polyalkyl complex is alkyl coupling. It is relatively uncommon but well established for the polymethyl derivatives, *fac*-$[PtMe_3L(L')_2]^+$ (L = tertiary phosphine),[293a] $PdMe_2(PEt_3)_2$,[293b] and $AuMe_3(PPh_3)$,[294] which cleanly eliminate ethane. In the first, two methyl groups trans to L′ couple more readily if L′ has a high "trans-influence", and L = L′. In the second, evidence suggests the two methyl groups must be cis to couple.

Coupling to give biphenyl is common for polyphenyl derivatives like $CrPh_3(S)_x$ (S = solvent). Much less commonly, polybenzyl compounds give bibenzyl. Evidence suggests that aryl coupling in early metal compounds is not necessarily analogous to the cis reductive elimination of methyl groups and may be much more complex.[13]

At some point during metal alkyl decomposition, an alkyl and hydride ligand are likely to be on the same metal. Their coupling is common, for example, as the final step in hydrogenation of activated olefins by dihydride complexes. A well-studied example is hydrogenation of activated olefins by $MoCp_2H_2$.[295] The intermediate hydrido-alkyl complex can sometimes be isolated and the reductive elimination reaction studied as a separate step (eq 12).



(12)

E. Homolytic M–C Bond Cleavage

Though metal alkyls like $PbMe_4$ decompose at high temperatures to give free alkyl radicals,[296] evidence that early transition metal alkyls decompose similarly at low temperatures is slight. Detection of coupling products is inadequate because they may arise in other ways. For example, decomposition of copper and silver propenyl complexes gives hexadienes with retention of configuration, suggesting the absence of free propenyl radicals.[297,298a] Yet free radical decomposition may take place under certain circumstances as in chlorinated solvents (see, for example, ref 299a). Some Cu[298b] and Ag alkyls also decompose by homolytic M–C bond cleavage, though probably not exclusively. The only satisfactory answer to this dilemma is to directly observe carbon based radicals or radical pairs (by ESR or CIDNP, respectively) on decomposition of a well-characterized metal alkyl. (The attempt to observe a benzyl radical on decomposition of $Zr(CH_2Ph)_4$ was unsuccessful.[73]) Experiments with radical trapping agents[299b] (see, for example, ref 299c) are less convincing since it is difficult to exclude the possibility that the trapping agent reacts with the metal complex and, in effect, initiates homolytic cleavage.[299d,e]

The postulate that the dissociation energy of the transition metal to carbon bond is significantly lower than that of a main group element is unsupported by estimates obtained so far [M–Me and M–Ph (M = Pt, Ti)[83,276,279]]. Metal-carbon bond force constants in $TiMeCl_3$[300] and $TiMe_4$[301] do not differ significantly from those in analogous main group compounds. Metal-carbon bond length also does not correlate well with stability.[140,226] A large number of early transition metal peralkyl complexes are now available and should permit resolution of this issue, for example, by calorimetric studies. Some of the first related experiments of this type have shown that the M–CH_3 dissociation energy in $M(CH_3)(CO)_5$ (M = Mn, Re) may, in fact, be on the order of that of M–CO.[299f]

VII. Reactions of Alkyl Complexes

Many transition metal alkyl reactions are similar to those of main group metal alkyls with some exceptions such as reaction with N_2 or SO_2. We survey briefly the common transition metal alkyl reactions[2,6,11] and emphasize examples within the early metal category. Fundamental reactions of metal alkyls from a mechanistic viewpoint can also be found in a recent book by Heck.[16b]

A. Electrophiles

Protonic reagents generally readily cleave the metal-alkyl bond to yield the alkane. In a few cases, e.g., $Cr(CMe_3)_4$, Ti(1-adamantyl)$_4$, and $[Cr(H_2O)_5R]^{2+}$, strong acids are required. In principle the proton may attack the metal, with RH formation by reductive elimination, or attack the alkyl carbon atom directly. A means of distinguishing between the two is not readily apparent. The former, in which the metal's *formal* oxidation state increases by two, does not seem possible for d^0 complexes such as WMe_6 or $Ti(CH_2CMe_3)_4$.

Lewis acids like BR_3, AlR_3, ZnR_2, or even MgX_2 (X = a halide) are often present after alkyl preparation or are added to "activate" the metal alkyl. Reactions between aluminum alkyls and transition metal halides have been extensively studied, yet most details remain obscure. A recent example is the reaction between $M(CH_2Ph)_4$ and $Al(CH_2Ph)_3$ (M = Zr, Ti).[65] When M = Zr a red crystalline product results which may contain bridging CH_2Ph groups. When M = Ti, however, no stable product was isolated, and toluene formed with time. Compare these results with the following proposal:[302]

$$Cp_2TiCl_2 + 2AlMe_3 \xrightarrow[\text{petrol}]{115°} Cp_2Ti(CH_2AlMeCl)_2 + 2CH_4$$

Since alkyls with few d electrons, like $TiMe_4(d^0)$, are also good Lewis acids, similar reactions (intermolecular α-hydrogen abstraction) may initiate decomposition:[265]

$$2TiMe_4 \rightarrow CH_4 + \text{"}Me_3Ti\text{"} + \text{"}TiMe_3(CH_2)\text{"}$$

Mechanistic details are not obvious.

B. Hydrogen

"Oxidative addition" is an attractive primary step for reaction of hydrogen with a transition metal alkyl:

$$R_xM + H_2 \rightarrow R_xMH_2$$

Reductive elimination gives RH:

$$R_xMH_2 \rightarrow RH + R_{x-1}MH \rightarrow R_{x-2}M + RH$$

Oxidative addition to d^0 complexes in this strict sense, however, seems impossible since higher oxidation states are unknown. Two reasonable alternatives are: (i) a catalytic amount of a lower valent metal complex forms by reductive elimination of R–R followed by addition of H_2 and redistribution, viz.

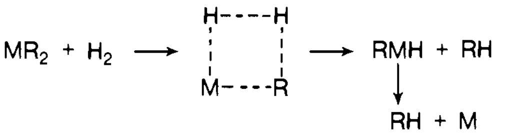
$$R_2M \rightarrow R\text{-}R + M$$

$$M + H_2 \rightleftharpoons MH_2$$

$$R_2M + MH_2 \rightleftharpoons 2RMH$$

$$2RMH \rightarrow 2RH + M$$

and (ii) hydrogen addition to M–R proceeds via a transition state in which only one end of the H_2 molecule is attached to the metal, viz.



Compare (ii) with the known reaction of LiPh with H_2 to give LiH and benzene. The reaction of hydrogen with the Li_3MPh_6 complexes almost certainly falls into this category. It is surprising in any case that the $M(CH_2Ph)_4$ complexes (M = Ti or Zr) "catalyze" olefin hydrogenation under conditions where they do not react with hydrogen.[65] However, since they also react with olefins, species which react more readily with hydrogen may form initially.

Hydrogen reactions are preparatively valuable in several instances. Hydrogen (1 atm) reacts with $TiCp_2Me_2$ in solution to give "titanocene", $Ti_2(C_{10}H_8)Cp_2H_2$.[303] In contrast, $ZrCp_2Me_2$ gives a dimeric crimson species postulated to be $(ZrCp_2Me)_2$,[189a] while $Ti(\eta^5\text{-}C_5Me_5)_2Me_2$ is stable toward H_2 under moderate conditions.[198] At 500 atm hydrogen reacts with $MMe_5(dmpe)$ (M = Nb or Ta) in THF in the presence of dmpe to give $MH_5(dmpe)_2$.[95]

C. Oxygen

The reaction of oxygen with metal alkyls to give the corresponding alkoxides has been known for many years. Brindley and Hodgson[304] recently studied its reaction with some selected metal alkyls, MR_4 (M = Ti or Zr, R = CH_2SiMe_3; M = Zr, R = CH_2Ph) and M_2R_6 (M = Mo, R = CH_2SiMe_3 or CH_2CMe_3; M = W, R = CH_2Ph). In hydrocarbons at 20 and −74° each rapidly absorbed 0.5 mol of O_2 per alkyl group. They postulated a radical chain mechanism propagated by alkylperoxy radicals:

$$R_nM + O_2 \rightarrow [R_nM{\cdot}O_2] \rightarrow R{\cdot}\ \text{(initiation)}$$

$$\left.\begin{array}{l} R{\cdot} + O_2 \xrightarrow{\text{fast}} RO_2{\cdot} \\ RO_2{\cdot} + R_nM \rightarrow RO_2MR_{n-1} + R{\cdot} \end{array}\right\}\ \text{(propagation)}$$

Peroxy transition metal alkyls were difficult to detect since they were rapidly converted to alkoxides. Nevertheless at 20° $Mo_2[CH_2CMe_3]_6$, $W_2(CH_2Ph)_6$, and $Zr(CH_2Ph)_4$ gave small amounts of peroxide. At −74° $Zr(CH_2Ph)_4$ and $W_2(CH_2Ph)_6$ gave 0.6 and 0.8 mol of peroxide per mole of metal, respectively. On hydrolysis the latter gave benzyl hydroperoxide. Only traces of peroxides were observed for the CH_2SiMe_3 and CH_2CMe_3 species. Phenothiazine retarded oxidation, consistent with the proposed free radical mechanism. The authors concluded that the hindered approach of peroxy radicals to vacant metal orbitals significantly slowed the reaction rate.

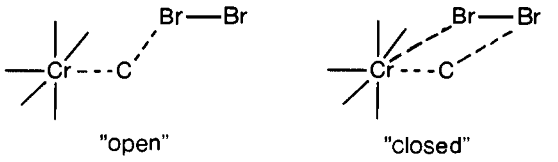
D. Halogens

Chlorine, bromine, and iodine commonly cleave the metal–carbon bond:

$$M\text{–}R + X_2 \rightarrow MX + RX$$

In one case,[305] $Mn(CO)_5R$, the configuration at carbon is reportedly retained, suggesting an initial oxidative addition of Br_2 to the metal followed by reductive elimination of RBr.

In contrast, Br_2 may attack the α carbon of R in $[Cr(H_2O_5)_5(R)]^{2+}$ directly to give a transition state of the "open" variety since kinetically stable $[Cr(H_2O)_5Br]^{2+}$ was not observed.[306] The bimolecular rate constants varied significantly with R, decreasing in the sequence Me > Pr > Et > CH_2CMe_3. Similar kinetic studies of the reaction of $[Cr(p\text{-}RC_6H_4)(H_2O)_5]^{2+}$ (R = Me, H, Br, CF_3, CN) with Br_2 and I_2 provided further support for the open transition state.[307]



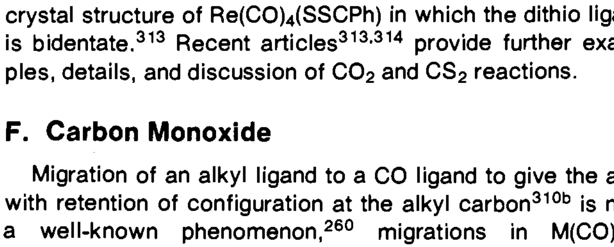
"open" "closed"

Several authors[308-310] found predominant inversion of configuration at carbon in other systems. It is possible that at least two cleavage mechanisms operate, the relative amount of each depending on the metal, halogen, ligands, and experimental conditons.

The possibility of free radical pathways should not be ignored. Certain alkyl halides oxidatively "add" to Ir(I)[311] or Pt(0)[312] by a free radical mechanism. A similar cleavage mechanism (by X_2) could be proposed. Interestingly, iodine reportedly does not react with $M(CH_2SiMe_3)_4$ (M = Ti and Zr) in the absence of oxygen.[304] Possibly a free radical pathway initiated by peroxyalkyl radicals predominates.

E. Carbon Dioxide and Carbon Disulfide

In the preparation of transition metal alkyls, CO_2 often is added at low temperatures to destroy excess Grignard or lithium reagent. A misconception that metal alkyls do not react with CO_2 has therefore arisen. While it is probably true that most transition metal alkyls do not react with CO_2 as readily as do Grignard reagents, several, especially the more highly alkylated ones, do react under mild conditions. For example, CO_2 reacts with $M(CH_2Ph)_4$ (M = Ti or Zr) at room temperature and atmospheric pressure (Zr > Ti).[65] Hydrolysis yields phenylacetic acid and tribenzylcarbinol in approximately equal amounts. In a second example CO_2 apparently reacts with the decomposition product[282b] (eq 13). Similar CS_2 "insertions" into a metal–alkyl bond are known as well as a crystal structure of $Re(CO)_4(SSCPh)$ in which the dithio ligand is bidentate.[313] Recent articles[313,314] provide further examples, details, and discussion of CO_2 and CS_2 reactions.



(13)

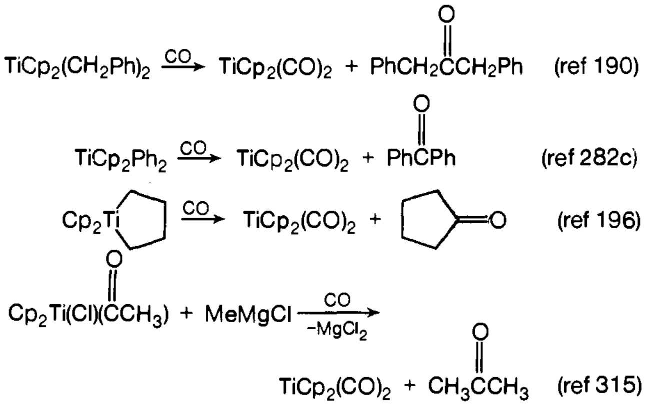
F. Carbon Monoxide

Migration of an alkyl ligand to a CO ligand to give the acyl with retention of configuration at the alkyl carbon[310b] is now a well-known phenomenon,[260] migrations in $M(CO)_5R$, FeCpLL'R (e.g., L = CO, L' = PPh_3), and $MCp(CO)_3R$ (M = Mo or W) being studied most thoroughly. Several early metal examples follow.

The reaction of CO with $TiCp_2(X)(R)$ (R = Me, CH_2Ph, X = Cl; R = Et, X = Cl, I) probably proceeds via $TiCp_2(X)(R)(CO)$ followed by migration of R to CO to give $TiCp_2(X)(COR)$ ($\nu_{C=O}$ = 1600–1625 cm^{-1}).[315] Decarbonylation of $TiCp_2(Cl)(COCH_2Ph)$ gave $TiCp_2(Cl)(CH_2Ph)$ essentially quantitatively at 40° in heptane in 0.5 h.

A similar reaction occurs between $NbCp_2Et(C_2H_4)$ and CO to give $NbCp_2(CO)(COEt)$[316] at high temperature and pressure, but $TaCp_2Me(CO)$ is unchanged at 80° in benzene under 1 atm of CO after 1 day.[95]

Acyl-alkyl complexes appear unstable with respect to further alkyl attack on the acyl:



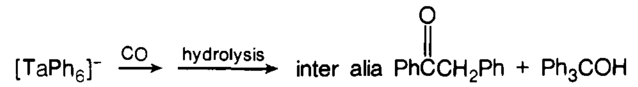
$$TiCp_2(CH_2Ph)_2 \xrightarrow{CO} TiCp_2(CO)_2 + PhCH_2\overset{O}{\overset{\|}{C}}CH_2Ph \quad \text{(ref 190)}$$

$$TiCp_2Ph_2 \xrightarrow{CO} TiCp_2(CO)_2 + Ph\overset{O}{\overset{\|}{C}}Ph \quad \text{(ref 282c)}$$

(ref 196)

$$Cp_2Ti(Cl)(\overset{O}{\overset{\|}{C}}CH_3) + MeMgCl \xrightarrow[-MgCl_2]{CO} TiCp_2(CO)_2 + CH_3\overset{O}{\overset{\|}{C}}CH_3 \quad \text{(ref 315)}$$

When more than two alkyl ligands are present, further reaction of the incipient ketone might be expected as in[134]



$$[TaPh_6]^- \xrightarrow{CO} \xrightarrow{\text{hydrolysis}} \text{inter alia } Ph\overset{O}{\overset{\|}{C}}CH_2Ph + Ph_3COH$$

The coordinated or free diketone, PhCOCOPh, is apparently reduced on hydrolysis. Products before hydrolysis may be complex; e.g., $Ta(C_8H_8)Me_3$ and $TaMe_5(dmpe)$ react with excess CO to give products with no infrared absorption characteristic of C≡O or C=O.[95] Metal-oxygen bonds may be present as in the reaction[317] of $Zr(CH_2Ph)_4$ and CO where Zr-O-C-Zr bonds had to be postulated; the authors could find no evidence for ZrC≡O or ZrCOR.

G. Nitric Oxide

An alkyl group also readily migrates to an NO ligand. NO (2 mol) reacts with $ZrCp_2Me_2$ or $ZrCp_2(Cl)(Me)$ to give monomeric species containing the *N*-methyl-*N*-nitrosohydroxylaminato ligand, $ZrCp_2[ON(Me)N{=}O](Cl \text{ or } Me)$.[189a] No further reaction occurred in several hours at higher temperatures. A similar but not monomeric product formed on reaction of 2 mol of NO with $TiCp_2Me_2$.

Hexamethyltungsten reacts with 4 mol of NO to give yellow $WMe_4[ON(Me)N{=}O]_2$ in essentially quantitative yield.[24] The crystal structure shows an eight-coordinate geometry somewhere between square-antiprismatic and dodecahedral[318] (Figure 10). The four oxygen atoms lie nearly in a plane while the four methyl groups do not; the CH_3'-W-CH_3' angle is 128.9°, the CH_3-W-CH_3 angle 100.2°. Its ^1H NMR spectrum in CD_2Cl_2 at room temperature shows two sharp singlets in a 4:2 ratio at τ 8.42 and 5.97, respectively, suggesting nonrigid behavior. Below −50° the τ 8.42 peak becomes two at τ 9.65 and 7.59. The highest observable peak in the mass spectrum was $WMe_3[ON(Me)N{=}O]_2^+$.

NO (4 mol) reacts with MMe_xCl_{5-x} ($x = 2$ or 3, M = Nb or Ta) to give *seven-coordinate* $MMe_{x-2}Cl_{5-x}[ON(Me)N{=}O]_2$.[319] The structure of the tantalum complex where $x = 3$ is a slightly distorted pentagonal bipyramid with the two chelating ligands and a methyl group in the pentagonal plane. The tantalum-carbon bond length, 2.248 Å, is not unusual.

H. Olefins and Acetylenes

The reactions of chromium alkyl and aryl species, some prepared in situ, with olefins,[272,273,320] dienes,[273,320,321] diphenylacetylene,[284,285,322-324] 2-butyne,[325-329] and acetylene[54] have been studied extensively. Olefins and dienes are isomerized and hydrogenated. With acetylenes, cyclic and linear condensation products in addition to products resulting from hydrogenation and alkyl or aryl transfer are found; e.g., see eq 14.[284c,323] Methyl complexes of Ti, Zr, V, Nb, Mo, and Mn give similar results[322] while phenyl groups transfer from $TiPh_4$ to PhC≡CPh[330] or $CrPh_3(THF)_3$ to HC≡CH.[54] In fact,

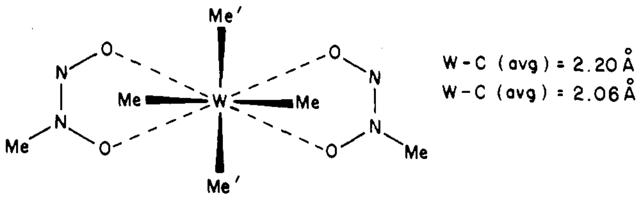
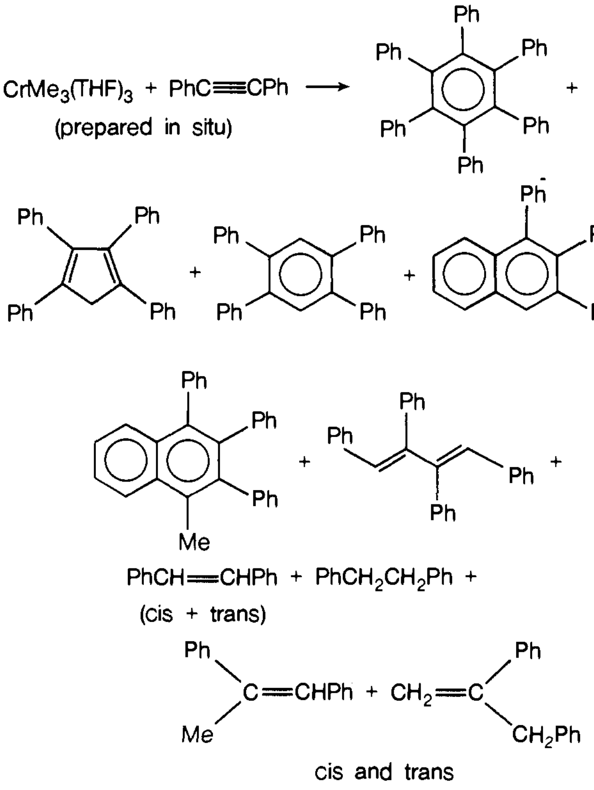


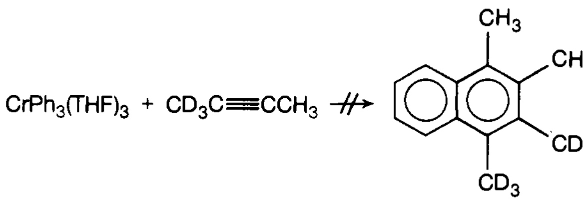
Figure 10. Schematic drawing of $WMe_4[ON(Me)N{=}O]_2$.



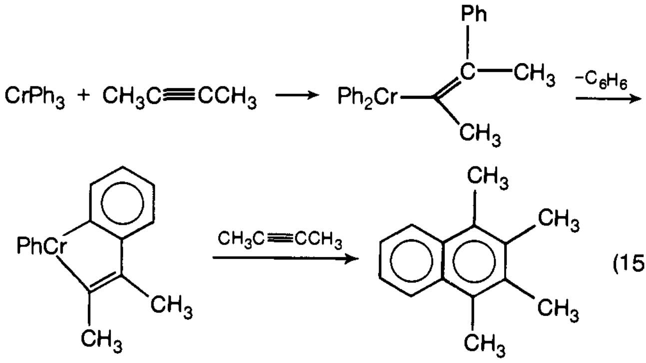
(14)

such findings are observed rather generally.[328,331] The interesting feature in this context is that the products incorporate methylene (formally), which is one reason why authors have postulated chromium-methylene complexes.[324] In one instance, $Fe(\eta^5\text{-}C_5H_5)(CO)_2R$, dimethyl acetylenedicarboxylate inserts into the Fe-R bond with retention of configuration at carbon.[310b]

Whitesides and Ehmann[328] studied the stoichiometric reaction of 2-butyne with $CrPh_3(THF)_3$, which yields, inter alia, 1,2,3,4-tetramethylnaphthalene. They excluded a free or metal-complexed tetramethylcyclobutadiene intermediate based on



Further labeling and kinetic isotope experiments and examination of relative yields of 1,2,3,4,5-pentamethylnaphthalene and 1,2,3,4,6-pentamethylnaphthalene employing $CrR_3(THF)_3$ (R = *o*-, *p*-, or *m*-tolyl) "demonstrates that a long-lived aryne-chromium complex is also not an intermediate in these cyclizations". Numerous other results led to the proposal (solvents omitted) in eq 15. The "chromocycle" intermediate is similar to the product of the reaction of $TiCp_2Ph_2$ with $PhC{\equiv}CPh$.[282c] In the reaction of 2-butyne with Cr(*o*-anisyl)$_3$, a related chromocycle forms by cleavage of methoxy from the ring.[325,326]



(15)

Alkyl ligand transfer to an olefin (or olefin "insertion") is comparatively difficult to study since it yields another alkyl ligand which similarly reacts with more olefin. If the first transfer occurs, then subsequent transfers are also likely. Alkyl chain growth in this manner is usually postulated in olefin polymerization by a transition metal catalyst, but details are still unclear. For example, the olefin may not need to π-bond to the metal before the alkyl transfers. Group 4 metal catalysts are most active, usually only in the presence of a cocatalyst like an aluminum alkyl, the function of which is uncertain. Recently, however, ethylene has been polymerized with $M(CH_2Ph)_4$ (M = Ti, Zr) and $CrRCl_2(THF)_3$ (R = Me, Et, etc.) in the absence of cocatalysts[171] (see also ref 56b). Perhaps the alkyl-olefin complex most similar to a postulated intermediate in an active system is $NbCp_2Et(C_2H_4)$,[221] but it only loses ethylene and gives $NbCp_2(H)(C_2H_4)$ on heating. Alkyl transfer to other unsaturated hydrocarbons like Cp (ref 213, 214) or C_8H_8[249] are probably poor models for the general reaction. Better models might be based on deVries' observation[153] that isobutylene reacts with $TiMeCl_3$ to give a product which on hydrolysis yields some neopentane. A second isobutylene "insertion" is probably sterically unfavorable.

Transfer of an aryl group to an olefin is basically different since an *alkyl* complex is formed which usually does not readily react with more olefin. In the case of Pd,[16b] rapid β-hydrogen elimination gives a new olefin, the aryl-substituted form of the starting olefin.

Two groups report the use of tungsten alkyls as olefin disproportionation catalysts. Hexamethyltungsten on alumina converts propylene to a mixture of ethylene and butenes[332,333] while tetrabenzyltungsten with $AlCl_3$ in benzene converts 2-pentene into a mixture of 2-butene and 3-hexene.[72a] In each case the alkyl complex almost certainly does not survive and the true catalyst is probably more closely related to group 6 disproportionation catalysts prepared in other ways (see, for example, ref 334).

I. Ketones

Since many main group alkyls like $ZnEt_2$, Hg(*p*-tolyl)$_2$, and $PbEt_4$ do not readily react with the carbonyl function like a Grignard reagent, a wide range of reactivities between transition metal alkyls and (e.g.) ketones should be expected. The Gilman test,[335] in which a metal alkyl adds to Michler's ketone, $(p\text{-}Me_2NC_6H_4)_2CO$, sometimes fails. For example, it is negative for $TiMeCl_3$[18] and $CrPh_2Cl$.[179] It is positive for binary alkyls except where steric crowding prevents ready addition. Though other factors or side reactions may conceivably be involved, the test results should indicate whether a given alkyl or aryl complex will react with ketones in general. Qualitatively, one might expect that the more powerful the alkylating agent which is required to prepare a given alkyl, the more readily the alkyl will react with the carbonyl function.

A study of the reaction of methylniobium and methyltantalum chlorides, primarily $NbMe_2Cl_3$, with ketones and aldehydes has recently appeared.[336a] Bulky ketones like $MeCOMe_3$ behave as donor ligands while a methyl group migrates to acetone or benzaldehyde to give an alkoxy ligand.

J. Other Reactions

A few other reactions should be mentioned.

Isocyanates "insert" into the metal-methyl bond in MMe_xCl_{5-x} (x = 1, 2, 3; M = Nb, Ta) to give acetamido complexes.[336b] With isonitriles, complexes containing $-C(Me){=}NR$ result. Each is a fairly general reaction.[337-339] When x = 2 and R = Me or Ph in RNCO, only $MCl_3[N(R)C(O)Me]_2$ species could be isolated in pure form while both $MMeCl_2[N(R)C(O)Me]_2$ and $MCl_2[N(R)C(O)Me]_3$ result when x = 3. In all cases the possibility that the substrate inserted into the M–Cl rather than M–Me bond could not be eliminated. Niobium complexes are considerably more unstable than those of tantalum and decompose near 25°.

Isothiocyanates react similarly to give products of the type $MCl_4[N(R)C(S)Me]$, $TaMeCl_3[N(R)C(S)Me]$, and $NbCl_3[N(Me)C(S)Me]_2$ (R = Me or Ph; M = Nb or Ta).[340] Thiocyanates, however, form simple adducts such as $MMe_2Cl_3(NCSMe)_2$. A crystal structure of $NbCl_3[N(Me)C(S)Me]_2$ shows two bidentate *N*-methylthioacetamide groups in the pentagonal plane of a pentagonal bipyramidal structure.

Carbodiimides, $RN{=}C{=}NR$ (R = Pr^i, Cy, or *p*-tolyl), react with MMe_xCl_{5-x} (M = Nb or Ta) to give complexes containing the $RN\text{-}\dot{C}(Me){=}NR$ ligand which, in at least one case, $TaMeCl_2[CyNC(Me){=}NCy]_2$, is bidentate[336c] as shown by x-ray studies. The reactivity sequence follows the order $MMeCl_4 > MMe_2Cl_3 > MMe_3Cl_2$, an order which holds also for the reactions discussed above.

Sulfur dioxide often reacts with group 4 metal alkyls to give O-bonded sulfinates in contrast to the more common S-sulfinates formed with group 8 metal alkyls.[341,342] With $TiCp_2R_2$ and $TiCp_2RX$ (R = alkyl or aryl; X = halide), monomeric $TiCp_2(O_2SMe)_2$, $TiCp_2(O_2SPh)_2$, and $TiCp_2Cl(O_2SMe)$ were formed.[343] In the latter, ^1H NMR evidence suggested isomers based on the mode of O_2SMe bonding. The reaction of SO_2 with $ZrCp_2MeCl$ did not give the expected product but one with the stoichiometry of a bis-SO_2 adduct postulated to be $ZrCp(O_2SC_5H_5)(O_2SMe)Cl$. Sulfur dioxide reacts with $TiMeX_3$ (X = Br, Cl), but the products have not been well characterized.[185]

$Zr(CH_2Ph)_4$ reacts with SO_2, PhNCO, and MeNCS to give $Zr(CH_2Ph)(O_2SCH_2Ph)_3$(O-sulfinate), $Zr[N(Ph)COCH_2Ph]_4$, and $Zr[N(Me)CSCH_2Ph]_4$, respectively.[77] It reacts with NO to give mixtures of the expected $ON(CH_2Ph)N{=}O$ complexes.

An intriguing reaction between molecular nitrogen and a phenyl ligand has been reported[344] (eq 16).

$$TiCp_2Ph_2 + 5LiPh \xrightarrow{N_2} PhNH_2 + NH_3 \text{ after hydrolysis} \quad (16)$$

0.03:0.17 mol per Ti at 1 atm

0.15:0.65 mol per Ti at 100 atm

A $TiN{=}NPh$ intermediate was postulated to account for these results. In the corresponding *o*-tolyl system, a mixture of all three isomeric toluidines resulted, which suggests isomerization possibly via benzyne-like intermediates during the course of the reaction (cf. ref 282a). A later study[335] showed LiPh was not necessary.

VIII. Abbreviations

acac	acetylacetonate
bpy	2,2-bipyridyl
Bu	*n*-butyl
Bu^i	isobutyl
Cp	η^5-cyclopentadienyl
Cy	cyclohexyl
diars	*o*-phenylenebisdimethylarsine
diox	*p*-dioxane
dme	1,2-dimethoxyethane
dmpe	1,2-bisdimethylphosphinoethane
dppe	1,2-bisdiphenylphosphinoethane
Et	ethyl
HMPA	hexamethylphosphoramide $[(\mathrm{Me_2N})_3\mathrm{P{=}O}]$
Ind	η^5-indenyl
Me	methyl
Mes	2,4,6-trimethylphenyl (mesityl)
Ph	phenyl
phen	*o*-phenanthroline
pip	piperidine
Pr	*n*-propyl
Pr^i	isopropyl
py	pyridine
pz	pyrazolyl
quin	quinoline
TEEDA	*N,N,N′,N′*-tetraethylethylenediamine
THF	tetrahydrofuran
TMEDA	*N,N,N′,N′*-tetramethylethylenediamine
TMMDA	*N,N,N′,N′*-tetramethylmethylenediamine
TMPDA	*N,N,N′,N′*-tetramethylpropylenediamine

IX. Addendum

In the period following completion of the manuscript, many significant findings have been reported. Perhaps the most interesting are reports by Schwartz et al. and by Schrock on the use of early transition metal alkyl compounds as potential reagents for organic synthesis.

Schwartz and coworkers[345] have recently developed synthetically useful reactions based on zirconium alkyls of the type $\mathrm{ZrCp_2(R)Cl}$. These are prepared by addition of olefins to $\mathrm{ZrCp_2(H)Cl}$, a reaction which was briefly explored by Wailes, Weigold, and Bell.[189b] The Zr atom migrates to the least hindered accessible position along the alkyl chain, probably by a series of Zr–H additions and eliminations. Cleavage reactions with HX, X_2 (X = Br, I), or acyl halides, or "insertions" with CO or O_2, thereby provide routes to alkyl halides, aldehydes, esters, acids, ketones, or alcohols. When R was *threo*- or *erythro*-$\mathrm{CHDCHDCMe_3}$, the configuration at the α-carbon atom was retained on cleavage with $\mathrm{Br_2}$ or on "insertion" of CO or $\mathrm{SO_2}$, while some racemization occurred on reaction with O_2.[345c] Oxidation of the zirconium alkyl derivatives with *tert*-butyl hydroperoxide followed by hydrolysis gave primary alcohols in high yield.[345d]

Similar interest pertains to alkylidene complexes of tantalum which are structural analogs of phosphorus ylides. The readily available[94] $\mathrm{(neopentyl)_3Ta{=}CHCMe_3}$ has been studied most thoroughly.[346a] It reacts with C=O functions to give olefins in much the same way as do phosphorus ylides, but the scope of the Ta=C reactions appears to be broader.

Simple methylene complexes of tantalum have now been prepared. The reaction of $\mathrm{TaMe_3Cl_2}$ with 1 or 2 mol of TlCp in toluene gave trimethyl compounds, $\mathrm{TaCpMe_3Cl}$ and $\mathrm{TaCp_2Me_3}$, respectively. In contrast similar reactions between $\mathrm{Ta(CH_2CMe_3)_2Cl_3}$ or $\mathrm{Ta(CH_2Ph)_3Cl_2}$ and 2 mol of TlCp provided alkylidene compounds (see section VI.B), $\mathrm{TaCp_2(CHCMe_3)Cl}$, and $\mathrm{TaCp_2(CHPh)(CH_2Ph)}$, respectively.[346b] Treatment of $\mathrm{TaCp_2Me_3}$ with $\mathrm{CPh_3{}^+BF_4{}^-}$ gave $\mathrm{[TaCp_2Me_2]^+BF_4{}^-}$, which, on deprotonation with base, gave the first definitive example of a transition metal-methylene complex, $\mathrm{TaCp_2(CH_2)(CH_3)}$. It is stable at room temperature but slowly decomposes in apparently a bimolecular fashion to give $\mathrm{TaCp_2(CH_3)(CH_2{=}CH_2)}$ and the fragment, "$\mathrm{TaCp_2(CH_3)}$", which reacts with L (L = $\mathrm{C_2H_4}$, CO, $\mathrm{PR_3}$) to give $\mathrm{TaCp_2(CH_3)L}$. Its reactions with $\mathrm{CH_3I}$ and $\mathrm{AlMe_3}$ suggest that the methylene carbon atom is nucleophilic. A crystal structure[347] showed the Ta-methylene bond length to be 2.026 (10) Å while ^{1}H NMR studies showed $\Delta G^{\ddagger}$ for the barrier to rotation about the $\mathrm{Ta{=}CH_2}$ bond to be ≥ 21.4 kcal mol^{-1}. In contrast, the $\Delta G^{\ddagger}$ values for carbene ligand rotation in $\mathrm{TaCp_2(CHCMe_3)Cl}$ and $\mathrm{TaCp_2(CHPh)(CH_2Ph)}$ are 16.8 ± 0.1 and 19.3 ± 0.1 kcal mol^{-1}, respectively.

Lappert, Patil, and Pedley[348] have measured the heats of alcoholysis of some titanium and zirconium complexes, $\mathrm{MR_4}$ (R = $\mathrm{CH_2SiMe_3}$, $\mathrm{CH_2CMe_3}$, or $\mathrm{CH_2Ph}$), $\mathrm{M(NR'_2)_4}$ (R = $\mathrm{CH_3}$ or $\mathrm{C_2H_5}$), and $\mathrm{MCl_4}$, and several hafnium analogs. The calculated "mean bond energies", $\bar{E}$(M–C), which varied from ca. 45 to 75 kcal mol^{-1}, can be taken as further evidence that the transition metal to carbon bond is not necessarily weak (see section VI.E). Close comparisons of $\bar{E}$(M–C) values, however, can be misleading because an alternative description of a particular M–C bond strength, the mean bond dissociation energy, $\bar{D}$(M–C), can be quite different from a particular $\bar{E}$(M–C), as in the case of R = $\mathrm{CH_2Ph}$.

Galyer, Wilkinson, and Lloyd[349] found the photoelectron spectrum of $\mathrm{WMe_6}$ and $\mathrm{TaMe_5}$ to be consistent with O_h and D_{3h} structures, respectively, in the gas phase. The spectrum reported by Cradock and Savage[26] is believed not to be that of $\mathrm{WMe_6}$.

Several new rhenium alkyls have been reported.[350] Volatile, red $\mathrm{ReOMe_4}$ is the product of a complex reaction between $\mathrm{ReOCl_3(PPh_3)_2}$ and methyllithium in diethyl ether in the presence of traces of molecular oxygen. An analogous reaction employing $\mathrm{Me_3SiCH_2MgCl}$ gave blue $\mathrm{ReO(CH_2SiMe_3)_4}$ and red $\mathrm{Re_2O_3(CH_2SiMe_3)_6}$. All are thermally stable and fairly unreactive toward water, dilute mineral acids, alcohols, $\mathrm{H_2}$, $\mathrm{CO_2}$, CO, and $\mathrm{SO_2}$. The ESR and electronic spectra of the monomers are consistent with square-pyramidal geometries.[351]

A brief communication described the isolation of thermally stable $\mathrm{MnR_2}$ complexes in which R = $\mathrm{CH_2CMe_3}$, $\mathrm{CH_2SiMe_3}$, and $\mathrm{CH_2CMe_2Ph}$.[352] They are apparently oxidized by molecular oxygen to give relatively unstable, green $\mathrm{MR_4}$ complexes analogous to Mn(1-norbornyl)$_4$.[98] A uranium complex, $\mathrm{Li_2U(CH_2SiMe_3)_6(TMEDA)_7}$, was also described. It is the first uranium alkyl containing more than one metal to carbon σ bond.

The preparation and properties of $\mathrm{W(CH_2Ph)_4}$[72a] have now been described more fully.[353] Red-brown $\mathrm{W(CH_2Ph)_4}$ is best prepared from $\mathrm{WCl_4}$ and $\mathrm{Mg(CH_2Ph)_2}$ in diethyl ether. It is sparingly soluble in common solvents and stable at room temperature. The authors also describe the preparation of olive-green $\mathrm{W(CH_2Ph)Cl_5}$ from $\mathrm{WCl_6}$ and $\mathrm{B(CH_2Ph)_3}$ in ether at −15 to −30°. Both form sparingly soluble bipyridyl adducts.

An expanded version of the original report[71] on isolable "$\mathrm{V(CH_2Ph)_4}$" has also appeared.[354] The black, low-melting crystals have the composition $\mathrm{V(CH_2Ph)_4(ether)}_n\mathrm{(dioxane)}_m$ where $n \geq 1$ and $m \geq 2$. The ESR signal at 77°K occurs at $g = 1.965$, in contrast to earlier results,[70] and no signal was found in ether or as a solid at 0°. "$\mathrm{V(CH_2Ph)_4}$" decomposes at 90° in ether to give 3.3–3.7 mol of toluene per V (cf. $\mathrm{Ti(CH_2Ph)_4}$ decomposition, section II.A.3) and a dark residue which gives $\mathrm{V(acetate)_3}$, $\mathrm{H_2}$, and toluene on treatment with acetic acid.

Fröhlich and coworkers have briefly described the preparation of yellow $\mathrm{Zr(CH_2Ph)_2(NPh_2)_2}$[355] and paramagnetic ($\mu$ = 1.54) $\mathrm{V(NEt_2)_3(C_2H_5)}$.[356] The former was prepared by addition of 1–2 mol of $\mathrm{HNPh_2}$ to $\mathrm{Zr(CH_2Ph)_4}$ and the latter by addition of LiC_2H_5 to $V(NEt_2)_3Cl$ in heptane. $V(NEt_2)_3(C_2H_5)$, a green liquid, appears to be thermally more stable than its Ti analog (see section V.C); it decomposes at ca. 115°.

The chemistry of organochromium compounds has been discussed thoroughly in a recent book by Sneeden.[357]

X. References

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