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HYDRIDE COMPOUNDS OF THE TITANIUM AND VANADIUM GROUP ELEMENTS

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I. Titanium, Zirconium, and Hafnium Hydrides

A. TITANIUM HYDRIDE COMPOUNDS

The current literature reflects the fact that molecular species containing a titanium–hydrogen bond are of much interest. This is, in part, due to their possible involvement in reactions involving unsaturated molecules such as alkenes, alkynes, hydrogen, carbon monoxide, and dinitrogen. However, such species remain elusive in many respects, and are often poorly characterized. Considerable progress has been made since the early 1960s, when reports of such compounds started to appear, but even now very few definitive X-ray (or neutron) diffraction studies are available because of the difficulty in obtaining suitable crystals of the air-reactive materials. Spectroscopic identification of Ti–H bonds is also frequently difficult to obtain. The intensity of absorptions associated with Ti–H stretching frequencies in infrared spectra is often low, and samples are often paramagnetic, being deriva-

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tives of Ti(III), so that ESR rather than NMR spectra must be used to infer the presence of such bonds. Relatively little use has been made of Raman spectroscopy, and the newer Fourier transform infrared techniques have not yet had time to make an impact on the problem. Chemical reactions, such as the release of hydrogen on treatment of the suspected hydride with acids and the conversion of CCl_4 into $CHCl_3$, have often been used as the means of detecting the Ti–H bond.

There has been no recent comprehensive review of this area, although a book on the organometallic chemistry of titanium, zirconium, and hafnium deals, in part, with some of the hydride derivatives (*1*). In the present review, the first part of the discussion reflects the fact that much of the early work on organotitanium hydrides was, often unknowingly at the time, interwoven with attempts to prepare titanocene, Cp_2Ti ($Cp = \eta^5\text{-}C_5H_5$). Subsequent sections deal with similar compounds containing an additional metal (e.g., aluminum), miscellaneous titanium hydride compounds, and a summary of the main properties of the above species.

1. Organo- and Cyclopentadienyl Titanium Hydrides

Four closely related species have featured prominently in the development of cyclopentadienyl titanium hydride chemistry, namely $[(\eta\text{-}C_5H_5)_2Ti]_{1-2}$, the so-called titanocene; the titanocene hydride $[(\eta\text{-}C_5H_5)_2TiH]_x$; the fulvalene-containing hydride $\mu\text{-}(\eta^5:\eta^5\text{-}C_{10}H_8)\text{-}\mu\text{-}(H)_2\text{-}[(\eta\text{-}C_5H_5)Ti]_2$; and the C_5H_4-bridged compound $(\eta\text{-}C_5H_5)_2Ti\text{-}\mu\text{-}(\eta:\eta^5\text{-}C_5H_4)\text{-}Ti(\eta\text{-}C_5H_5)$. The nature of the first two of these compounds remains uncertain even now, and related derivatives have often been prepared to assist in characterizing this type of compound. It now appears likely that several of the early experiments designed to prepare titanocene, Cp_2Ti, did in fact lead to the fulvalene titanium hydride derivative, although it should be stressed that this remains to be proved in several cases. In view of this fact, the early chemistry of titanocene-type compounds is reviewed first, in order to clarify the relationship between the different types of compounds described in the various reports.

An air-sensitive, dark-green, diamagnetic crystalline solid, obtained by treating titanium dichloride with NaC_5H_5 in tetrahydrofuran (THF), was reported to be titanocene, $(C_5H_5)_2Ti$, as early as 1956. The compound was easily oxidized to the cation $[(C_5H_5)_2Ti]^+$ and formed an adduct with THF, $(C_5H_5)_2Ti \cdot THF$, that exists as a green paramagnetic solid at low temperatures, and quickly transforms to a brown diamagnetic solid at 25°C (*2*). A similar green solid was obtained by

Clauss and Bestian (*3*) when $Cp_2Ti(CH_3)_2$ in hexane at 20°C was subjected to an atmosphere of hydrogen, but the solid was formulated by these authors as a dimeric species $[(C_5H_5)_2Ti]_2$.

Attempts to repeat these experiments did not immediately clarify the situation, since products were often incompletely characterized. The use of Na/Hg amalgam (*4, 5*), Na/naphthalene (*6, 7*), and sodium sand (*8*) in reactions (1), (2), and (3) also led to volatile green solids, again formulated as dimeric species

$$Cp_2TiCl_2 + 2NaHg \xrightarrow{C_6H_5CH_3} [(C_5H_5)_2Ti] + 2NaCl + 2Hg \tag{1}$$

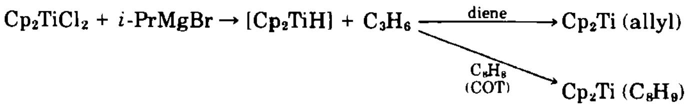
$$Cp_2TiCl_2 + 2NaC_{10}H_8 \xrightarrow{THF} [(C_5H_5)_2Ti] + 2C_{10}H_8 + 2NaCl \tag{2}$$

$$Cp_2TiCl_2 + 2Na \xrightarrow{C_6H_5CH_3} [(C_5H_5)_2Ti] + 2NaCl \tag{3}$$

$[(C_5H_5)_2Ti]_2$, and the unexpected diamagnetism was confirmed. A further unusual feature, deduced from infrared spectral data, was that in one case the compound was not of the π-sandwich type, but instead the dimer apparently contained both π- and σ-bonded cyclopentadienyl groups (*8*).

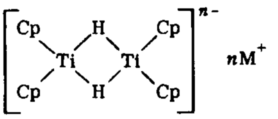
The precise nature of "titanocene" therefore remained uncertain up to the late 1960s, although other reports appeared to be consistent with the presence of the $(C_5H_5)Ti$ unit in some form in the various reaction mixtures. Thus the green solution, obtained as in reaction (2), absorbed carbon monoxide slowly to give the known dicarbonyl, $Cp_2Ti(CO)_2$, and although the green solution did not react with 2,2′-dipyridyl, the monomeric, blue-black $Cp_2Ti(dipy)$ compound was obtained by the action of dilithium dipyridyl on Cp_2TiCl_2. However, even at this stage doubts were expressed as to whether titanocene was a simple ferrocene-like molecule (*9*). A series of experiments also identified an "active titanocene," prepared as in Eq. (2), as a dinitrogen fixing reagent, with $[(C_5H_5)_2Ti]_2N_2$ as the intermediate (*10, 11*). Experiments related to those above have also claimed to have trapped Cp_2Ti as the Cp_2Ti(2-bipyrydyl) complex when Cp_2TiMe is reacted with aromatic amines (*12*), and Cp_2Ti is also stabilised by bridging pyrazolyl groups as in $(Cp_2Ti)_2(\mu\text{-pyrazolyl})_2$ (*13*).

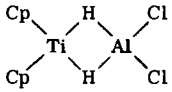
Meanwhile, other reports indicated the presence of titanium hydride species in many reduced Ti(IV) solutions. As early as 1966, Brintzinger suggested on the basis of ESR measurements, that a hydride was present in the dark brown solutions obtained from the action of EtMgCl on Cp_2TiCl (*14*) and this was later identified using ESR as the anion $(Cp_2TiH_2)^-$, which may also be obtained using magnesium/THF or isopropyllithium as the reducing mixture (*15*). A neutral hydride was also postulated as an intermediate, but not isolated, in the reactions (*16, 17*):



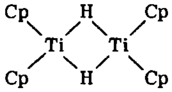
$$\begin{aligned} Cp_2TiCl_2 + i\text{-}PrMgBr \rightarrow [Cp_2TiH] + C_3H_6 &\xrightarrow{\text{diene}} Cp_2Ti\,(\text{allyl}) \\ &\xrightarrow[(\text{COT})]{C_8H_8} Cp_2Ti\,(C_8H_9) \end{aligned}$$

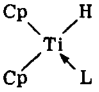
A related series of anionic $\{[Cp_2Ti(\mu\text{-}H)_2TiCp_2]^-M^+$, where M = Li, Na, **(I)**$\}$ and neutral $[Cp_2TiH_2M$, where M = MgBr, $AlCl_2$, AlH_2, **(II)**$]$ hydrides, first reported by Olivé *et al.* (*18, 19*), have also been partially characterized from line-width trends in their ESR spectra (*20, 21*).


(I)

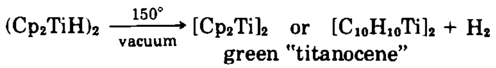

(II)

A series of investigations by Brintzinger and Bercaw in the early 1970s largely clarified the relationship between these titanocene and hydride derivatives. The first isolated hydride, Cp_2TiH, was obtained as a violet solid by treating Cp_2TiMe_2 with hydrogen at low pressure in the *absence* of solvent (*22*). Under these conditions, only traces of the green "titanocene" referred to be Clauss and Bestian (*3*) are formed. Since the hydride was diamagnetic a dimeric structure **(III)** was proposed, and cleavage of the $Ti(\mu\text{-}H)_2Ti$ unit by ligands (THF, PPh_3) yields the paramagnetic species **(IV)**. The hydride is apparently only an intermediate, since it decomposes at 150°C in *vacuo* to the green "titanocene" reported earlier.


(III)


(IV)

(L = THF or PPh_3)

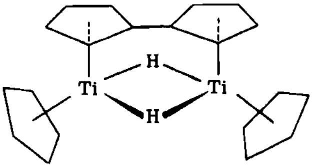


$$(Cp_2TiH)_2 \xrightarrow[\text{vacuum}]{150^\circ} \underset{\text{green "titanocene"}}{[Cp_2Ti]_2 \text{ or } [C_{10}H_{10}Ti]_2} + H_2$$

It also transforms slowly into a gray-green isomer on standing at room temperature (*22*). This isomer was subsequently suggested to be a polymeric form of the hydride, $(Cp_2TiH)_x$, and is interesting in that on stirring in toluene at 20°C this is also unstable and evolves 0.5 mol of H_2 per mole of Ti with the formation of a dark-colored solution (*23*).

While the solution species must therefore be formulated as $(Cp_2Ti)_x$, it has been shown to be dimeric in benzene. Although the degree of association in the solid state is uncertain, the infrared spectra of the solid and solution species are similar, but different from that of $(Cp_2TiH)_x$. It is noteworthy that a toluene solution containing $(Cp_2Ti)_2$ is paramagnetic and forms a bright green adduct with THF that decomposes quickly to a brown solid. Such behavior is comparable with that in the initial report claiming the preparation of titanocene (*2*). The dark-colored solid and solution, initially called "metastable" titanocene, is different from, but isomeric with, the green titanocene. It is a much more reactive compound than the latter, and it is transformed into the green form by heating in toluene at 100°C (*23*).

The early 1970s also saw the resolution of the problem regarding the precise nature of the green "titanocene" $(C_{10}H_{10}Ti)_2$. While several reports had indicated that treatment of "titanocene" with hydrogen chloride gas did not afford Cp_2TiCl or Cp_2TiCl_2, it was Brintzinger and Bercaw who established that the product of this reaction was in fact $(C_{10}H_9TiCl)_2$ (*24*). Since the infrared spectrum of "titanocene" contains a strong band at 1230 cm^{-1} that is absent in $(C_{10}H_9TiCl)_2$, Brintzinger and Bercaw suggested that this arises from a $Ti(\mu\text{-}H)_2Ti$ group, and formulated titanocene, $(Cp_2Ti)_2$, as a fulvalene derivative $[Cp(C_5H_4)TiH]_2$ or $(CpTiH)_2(C_{10}H_8)$ (V).



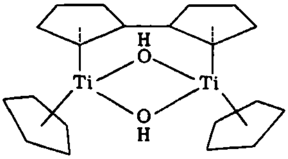
(V)

Although this proposal has not been verified by X-ray crystal data, since suitable crystals have not yet been obtained, there are structural data available on closely related compounds. The hydride (V) is hydrolyzed by water to the bis(hydroxy) derivative (VI), which crystallizes from THF solution as the bis solvate.

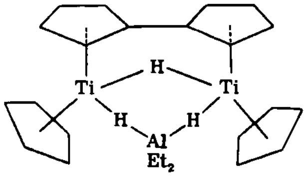
$$(CpTiH)_2(C_{10}H_8) + 2H_2O \xrightarrow{THF} \underset{(VI)}{(CpTiOH)_2(C_{10}H_8)} \cdot 2C_4H_8O$$

The crystal structure of (VI) confirms the presence of a π-bonded fulvalene, with hydroxy groups bridging the two titanium atoms, and the THF hydrogen-bonded to the hydrogens of the hydroxy groups (*25*).

The Ti–Ti separation (3.195 Å) leaves open the question of how much Ti–Ti interaction is present, and it is significant that the compound is weakly paramagnetic. The presence of a π-bonded fulvalene has also been found in other systems, namely, the mixed aluminotitanium hydrides $(CpTi)_2(H)(H_2AlEt_2)(C_{10}H_8)$ (*26*) (VII), and $[(C_5H_4)TiHAlEt_2]_2$ $C_{10}H_8)$ (*26, 27*), which are discussed further below, and the niobocene $(CpNbH)_2(C_{10}H_8)$ (*28*). In addition the ^{13}C-NMR spectrum of titanocene confirms the presence of a fulvalene group by comparison with the $(\eta^5:\eta^{5'}$-fulvalene)dicobalt(III,III) dication (*29*). With the structure of the green "titanocene" therefore established it is very probable that many of the previous formulations as $[(C_5H_5)_2Ti]_2$ require modification (e.g., Refs. *2–8*) although some intriguing uncertainties remain. For example, the green titanocene $(Cp_2TiH)_2(C_{10}H_8)$ is relatively unreactive, but the isomeric "metastable" dark form, referred to above as $[(C_5H_5)_2Ti]_x$, reacts rapidly as the dimer in toluene or ether solution with CO and N_2 forming $Cp_2Ti(CO)_2$ and $[(C_5H_5)_2Ti]_2N_2$, respectively (*23, 30*). A more complex reaction occurs with hydrogen, and the hydride species formed have not been fully identified (*23*).



(VI)

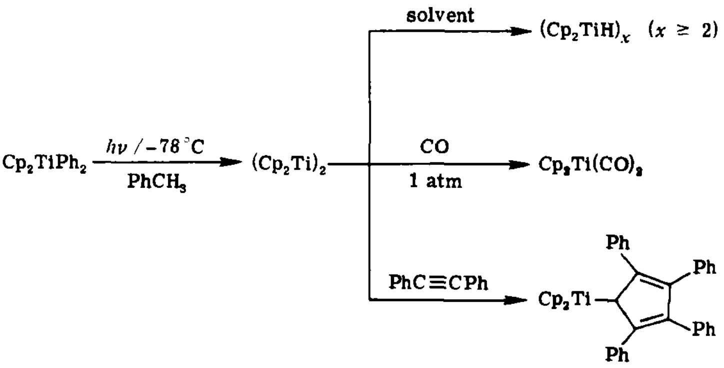


(VII)

Although another active form of titanocene, formulated as $[(C_5H_5)_2Ti]_{1-2}$, has been obtained by van Tamelen *et al.*, it was suggested that this may very well be identical to the metastable form (*31*). More recently, a black solid active form of titanocene, also formulated as $C_{10}H_{10}Ti$, has been obtained from the diphenyl derivative Cp_2TiPh_2 by photolysis in benzene (*32, 33*). One report suggests that the titanocene is similar to that obtained earlier from Cp_2TiMe_2 (see Ref. *32*), and although the product was not fully characterized it does not show any bands in its infrared spectrum between 1230 and 1220 cm^{-1} from any Ti–H–Ti group vibration (*32*). An ESR spectrum of another similar product suggests a solution equilibrium as

$$Cp_2Ti(solv)_2 \xrightleftharpoons{THF} 2Cp_2Ti(solv)$$

and continuing the photolysis leads to $Cp_2TiH \cdot THF$, as well as $(Cp_2TiH)_x$ (*33*). An overall reaction scheme has been proposed:



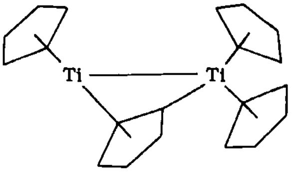
No suggestions have yet been made as to either the precise structures of these active forms or how they differ from the more stable green fulvalene form. Several attempts have been made to prepare similar species by electrochemical reduction of Cp_2TiX_2 and $CpTiX_3$ compounds (e.g., Ref. *30*, and references therein). Blue solutions have been obtained, but the identity of the species at present remains uncertain, although recent studies have indicated that anionic species are the probable products in THF solution according to Refs. *34–36:*

$$
\begin{gathered}
Cp_2TiX_2 + e^- \rightleftharpoons [Cp_2TiX_2]^- \\
[Cp_2TiX_2]^- + e^- \rightleftharpoons [Cp_2TiX_2]^{2-} \\
[Cp_2TiX_2]^{2-} + e^- \rightleftharpoons [Cp_2TiX_2]^{3-} \\
[Cp_2TiX_2]^{2-} \rightarrow [Cp_2TiX]^- + X^-
\end{gathered}
$$

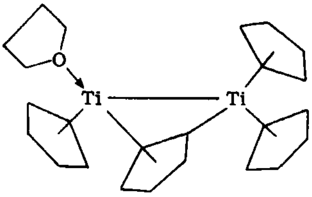
where X = Cl, Br, alkyl, aryloxy. However, it has also been reported that controlled reduction of Cp_2TiCl_2 in dimethoxyethane under an atmosphere of CO results in a high yield of $Cp_2Ti(CO)_2$, so that (Cp_2Ti) may be produced at some stage in the reduction (*23*).

While it is not the purpose here to review all Cp–Ti compounds, there is obviously a very close relationship between CpTi moieties and their rearrangement product $(C_5H_4)TiH$ via ring-to-titanium α-hydrogen shift, as has been alluded to above. The nature of the Ti–H species involved in reactions between low-valent titanium compounds and dinitrogen is not always clear. There seems little doubt that some form of bis(cyclopentadienyl) titanium is an active intermediate in dinitrogen coordination reactions (*31, 37–39*), but there is as yet no conclusive evidence that a Ti–H species is involved in the initial reaction (*11*), despite some claims to the contrary (*40*). The existence of different forms of Cp_2Ti is referred to again below.

Further information on the products of reduction of Cp_2TiCl_2 with potassium naphthalene in THF has been elicited by carrying out the reaction at −80°C. Removal of the solvent at room temperature followed by extraction with toluene yields $(C_5H_5)_3(C_5H_4)Ti_2$ (**VIII**) as a black powder. Although crystals of this material suitable for X-ray analysis could not be obtained, the structure of the THF adduct, $(\eta\text{-}C_5H_5)_2\text{-}Ti\text{-}\mu\text{-}(\eta^1:\eta^5\text{-}C_5H_4)\text{-}Ti\text{-}(\eta\text{-}C_5H_5)(C_4H_8O)\text{-}(C_4H_8O)$ (**IX**), shows the existence of a Ti–Ti bond, with one THF molecule occupying a lattice site. Since (**IX**) is converted to a pure form of (**VIII**) by removal of the THF under vacuum at room temperature, it has been suggested that the structures of (**VIII**) and (**IX**) are similar (*41, 42*).

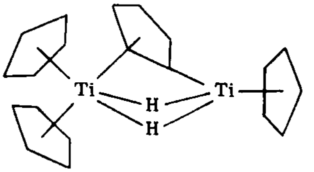


(**VIII**)

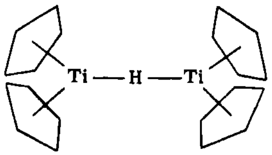


(**IX**)

The black solid (**VIII**) is converted into the green fulvalene titanocene (**V**) at 110°C, and also reacts with H_2, N_2, and alkenes (*42*), as do the active metastable forms of titanocene (*30*). With hydrogen, (**VIII**) yields a green-gray precipitate, formulated as $[(C_5H_5)_3(C_5H_4)Ti_2]\cdot H_2$, from toluene solution. The infrared spectrum and deuteration studies show this solid to contain a Ti–H bond, probably with the hydrogen in a bridging position, as either



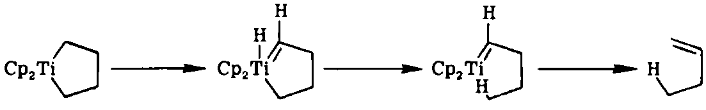
or



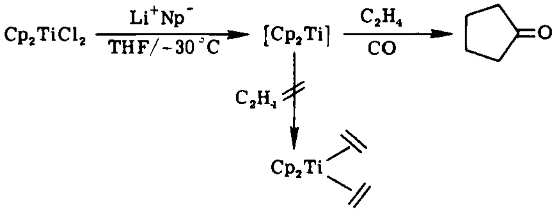
$$(C_5H_5)_3(C_5H_4)Ti_2 + H_2 \underset{\text{vacuum}}{\overset{H_2\ 1\text{–}10\ \text{atm}}{\rightleftharpoons}} [(C_5H_5)_3(C_5H_4)Ti_2]\cdot H_2$$

The solid evolves 1 mol of hydrogen per mole of (**VIII**) used, under vacuum, and is therefore similar to the green-gray metastable polymeric form of titancene discussed above and formulated as $(Cp_2TiH)_x$ (*23*). This solid evolves only 0.5 mol of hydrogen per mole of Ti under vacuum, but both solids show an infrared absorption at 1140 cm^{-1} from the Ti–H bond, as opposed to an absorption at 1450 cm^{-1} from the $Ti\text{-}\mu\text{-}(H)_2\text{-}Ti$ group in the violet $(Cp_2TiH)_2$ (*22*). Thus although the two green-gray solids are similar, further properties of each are required before their relationship can be considered as established.

The metallocycle 1,4-tetramethylene bis(cyclopentadienyl)titanium(IV), obtained by reacting $CpTiCl_2$ with $Li(CH_2)_4Li$, decomposes at −30°C, yielding a mixture of 1-butene and ethylene (*43*). The pathway leading to 1-butene may involve a hydride intermediate, although whether this is formed by α- or β-hydrogen atom elimination is uncertain, e.g.,



Assuming carbon–carbon bond cleavage occurs in the route leading to ethylene formation, unsuccessful attempts have been made to isolate the bis(ethylene) intermediate by reacting ethylene with titanocene obtained in a way similar to that described above (*41*). However, carbonylation of the reaction mixture yielded cyclopentanone, inferring that titanocene intermediates are produced (*43*).

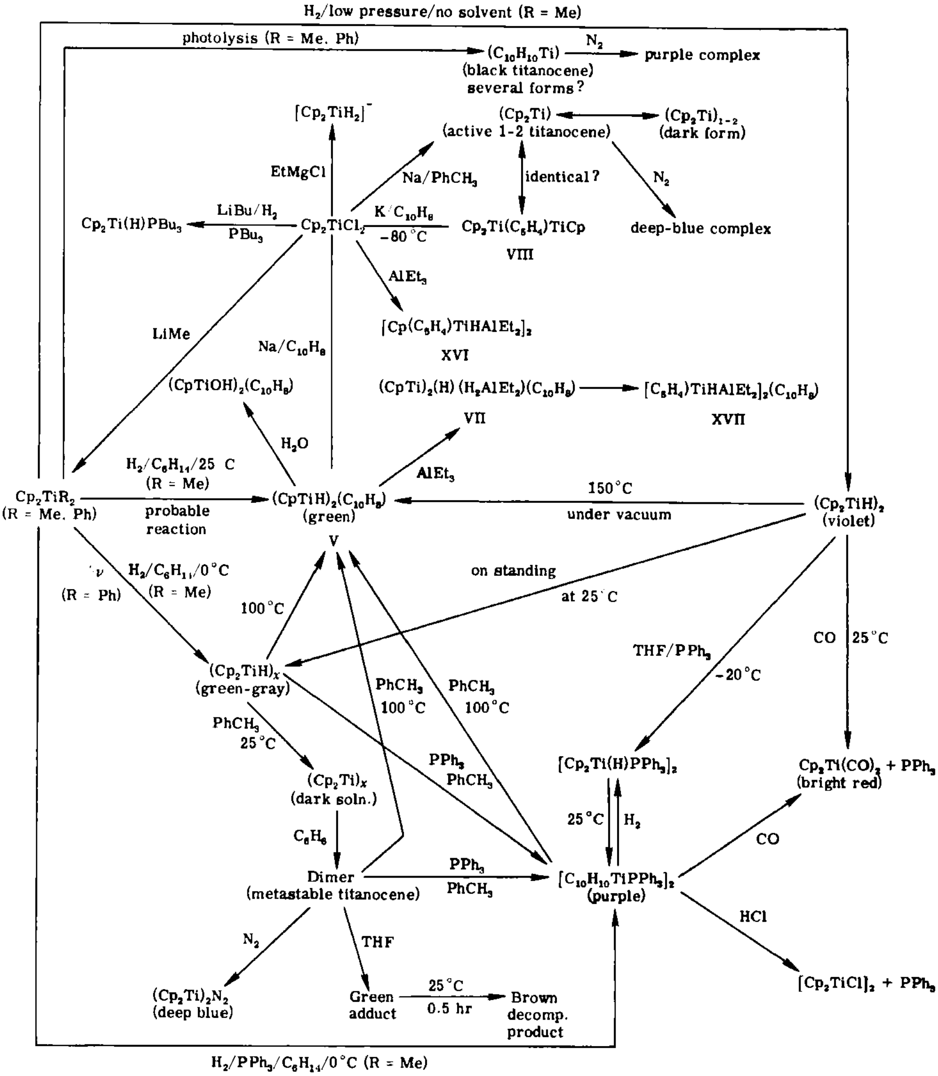


In conclusion, it cannot be assumed at present that all compounds previously formulated as $(C_5H_5)_2Ti$ are in fact (**VIII**); subtle differences between the various compounds still remain.

A summary of the reactions involving the cyclopentadienyl titanium hydrides is given in Scheme 1 (page 276).

Successful attempts have been made to classify the nature of some of the above species by the use of the pentamethylcyclopentadienyl group, $C_5Me_5(Cp^*)$, which it was supposed avoided the possibility of hydrogen transfer from the Cp* ring to the metal. Using this modification it has been possible to obtain pure monomeric Cp^*_2Ti as described below; this is now best prepared from its dinitrogen complex, through a series of equilibria (*39, 44*):

$$2Cp^*_2Ti \underset{\text{vacuum}}{\overset{N_2}{\rightleftharpoons}} [Cp^*_2Ti]_2N_2 \underset{\text{vacuum}}{\overset{2N_2}{\rightleftharpoons}} [Cp^*_2TiN_2]_2N_2$$



SCHEME 1.

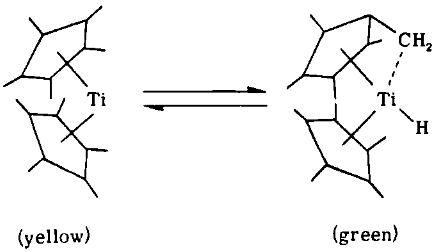
This route is necessary since initial attempts to prepare Cp_2^*Ti led to mixtures. Thus while $Cp_2^*TiMe_2$ does not react appreciably with hydrogen (in contrast to Cp_2TiMe_2) when it is refluxed in toluene solution, methane is evolved and a turquoise solid $(Cp^*)(C_5Me_4CH_2)TiMe$, is formed. This solid does react with hydrogen, yielding the diamagnetic dihydride $Cp_2^*TiH_2$, which dissociates in hydrocarbon solvents under vacuum at room temperature to exist in equilibrium with Cp_2^*Ti and Cp_2^*TiH, both of which appear to be monomeric in solution (*23, 39*).

$$(Cp^*)(C_5Me_4CH_2)TiMe + 2H_2 \rightarrow Cp_2^*TiH_2 + CH_4$$

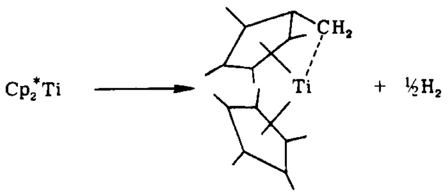
$$Cp_2^*TiH_2 \rightleftharpoons Cp_2^*Ti + H_2$$

$$Cp_2^*TiH_2 + Cp_2^*Ti \rightleftharpoons 2Cp_2^*TiH$$

Passage of dinitrogen into this mixture precipitates the dinitrogen complex as a blue-black microcrystalline solid, and thus provides a synthesis of pure Cp_2^*Ti. The yellow-orange Cp_2^*Ti turns yellow-green in solution, and NMR measurements on the paramagnetic Ti(II) species have led to suggestions of the tautomerism:

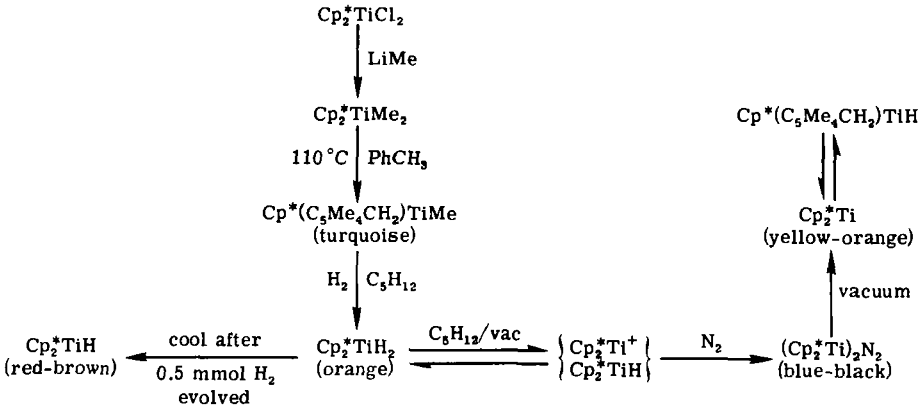


On prolonged standing at room temperature, Cp_2^*Ti slowly evolves hydrogen yielding the dark violet monomeric $(Cp^*)(C_5Me_4CH_2)Ti$ (*39*).



Although relatively few further investigations have been made on these compounds, they nicely illustrate the significantly different chemistry that emerges with the use of the C_5Me_5 ligand. The various reactions are summarized in Scheme 2 (page 278).

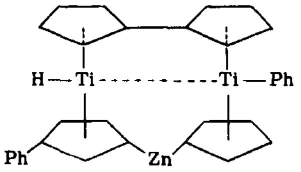
Thus the ring-to-titanium α-hydrogen shift, noted above for the C_5H_5Ti moiety, persists even for the C_5Me_5 ring. Confirmation of the fact that the cyclopentadienyl ligand acts as a hydrogen source was also obtained in studies on the dinitrogen-fixing system $Cp_2TiCl_2/Mg/MgI_2$ using deuterated solvents and the C_5D_5 ligand (*45*).



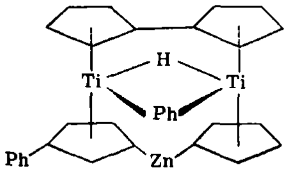
SCHEME 2.

2. *Miscellaneous* Ti–H *Compounds*

The formation of $Cp_2Ti(H)(PPh_3)$ from $(Cp_2TiH)_2$ has been referred to above (Scheme 1). A similar derivative $Cp_2Ti(H)(PBu_3)$ has been detected by ESR measurements when the phosphine is added to a mixture of $Cp_2TiCl_2/LiBu/H_2$ in toluene solution. Such mixtures are hydrogenation catalysts, and the active species has been suggested to be Cp_2TiH existing in a monomer–dimer equilibrium. A complex reaction occurs when Cp_2TiPh_2 is heated with $ZnPh_2$ in ethereal solvents or toluene solution; benzene is evolved and a dark violet diamagnetic solid precipitates. Although neither mass nor NMR spectra could be obtained, other data suggested the solid contained the Ti–H group and a Ti–Ti bond as in (X) or (XI) (*46*).



(X)

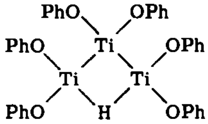


(XI)

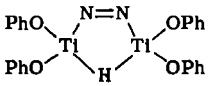
In contrast to this reaction, the action of the fulvalene titanocene **V** or the complex **VIII** on $ZnPh_2$ results in decomposition of the latter to metallic zinc and benzene. Similar decompositions are observed for $HgPh_2$ (*47*) and $ZnEt_2$ (*48*).

A series of hydrides of empirical formula $Me_2P(CH_2)_2PMe_2MH_3$ (M = Ti, Zr, or Hf) have been prepared from the tetrabenzyl metal compounds by reaction with the phosphine ligand under a high pressure

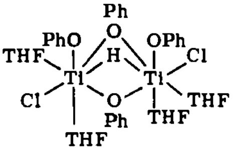
(200–400 atm) of hydrogen. The compounds appear to be polymeric species containing M–H–M bridge bonds (*49*). Another interesting series of hydrides has been reported by Wilkinson *et al.*, arising from reduction of $[Ti(OPh)_2Cl_2]_2$ using either sodium amalgam (or potassium metal) or sodium borohydride (*50*). With the former, $[Ti(OPh)_2]_3H$ is formed under argon as an air-sensitive gray powder, and has been assigned the probable structure (**XII**). If the reaction is carried out under nitrogen, the purple complex $[Ti(OPh)_2]_2(N_2)H$ results, and the structure (**XIII**) has been suggested. The action of the borohydride in THF solution leads to a yellow solid that also appears to contain a bridging hydride Ti–H–Ti group in $[Ti(OPh)_2Cl(THF)_2]_2H$ (**XIV**).



(XII)



(XIII)

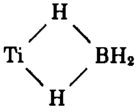


(XIV)

A compound similar to (**XIII**) has also been prepared from the pyrocatechol compound $Ti(O_2C_6H_4)Cl_2$ by reduction with sodium amalgam in THF, and has been formulated to be similar to (**XIII**) with the two phenoxide groups at each titanium being replaced by the pyrocatecholate dianion. The ESR signal from both these complexes suggests the presence of one unpaired electron per dimer (*50*).

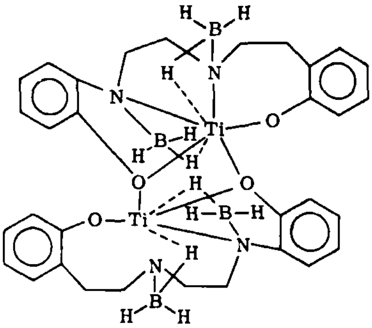
3. *Hydrides Bridging with Other Elements*

Several compounds containing Ti–H–M bonds are well known, in particular those containing a BH_4 or AlH_4 group. Since the former compounds have been reviewed recently (*51*), only brief mention is made of them here, but the Ti–H–Al compounds are discussed in more detail. The mode of attachment of the BH_4 group to the titanium atom is established, in compounds such as Cp_2TiBH_4, to be through a double hydrogen bridge



and recent electron diffraction results indicate that a similar model persists in the gas phase (*52*). An unusual Ti–H–B interaction occurs in the dimeric compound $[C_{16}H_{16}N_2O_2Ti(BH_3)_2]_2$. Here, two BH_3 groups are coordinated to nitrogen atoms in the *NN′*-ethylenebis(salicylidenaminato) ligand, and also interact, through Ti–H–B bonds, with each metal center, as in (**XV**), forming a capped octahedral arrangement around each titanium atom (*53*). The unstable borohydride $Ti(BH_4)_3$ has recently been prepared by grinding solid $TiCl_4$ and $LiBH_4$ together at low temperatures. It decomposes at 20°C, but can be stabilized as the THF adduct $Ti(BH_4)_3 \cdot 2THF$ (*54*).

$$TiCl_4 + LiBH_4 \rightarrow Ti(BH_4)_3 \rightarrow TiB_2 + 0.5B_2H_6 + 4.5H_2$$

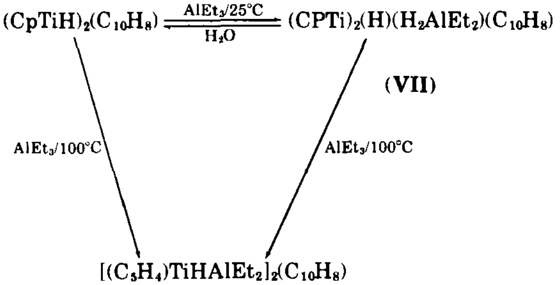


(**XV**)

Ti–H–Al *compounds.* Some of these have been briefly referred to above—e.g. (**VII**)—and a novel series of related compounds, (**XVI**) and (**XVII**), has been obtained by a series of reactions (*26, 27, 55*):

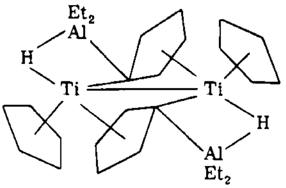
$$\left.\begin{matrix} Cp_2TiPh_2 \\ Cp_2TiCl_2 \\ Cp_2TiCl \end{matrix}\right\} \xrightarrow{AlEt_3} [Cp(C_5H_4)TiHAlEt_2]_2$$

(**XVI**)

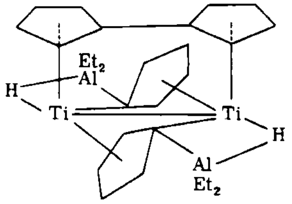


(**XVII**)

The structure of the reddish-purple (**VII**) has been given (Section I,A,1). Compound (**XVII**) is similar in that it also contains the fulvalene ligand, but it is unlike (**VII**) in that it possesses a Ti–Ti bond. On the other hand, both (**XVII**) and (**XVI**) are more reminiscent of the compound that is possibly related to the "active" form of titanocene, containing both bridging (C_5H_4) groups and Ti–Ti bonds. However, it is clear that a close structural relationship exists among all three compounds, the two Cp ligands in (**XIV**) being replaced by the fulvalene ligand in (**XVII**). It has not yet been reported whether it is possible to convert (**XVI**) to (**XVII**), but such a transformation would appear feasible, especially in view of the relationship among $(Cp_2Ti)_2(H)(H_2AlEt_2)(C_{10}H_8)$, (**VII**), and (**XVII**) mentioned above. These reactions are obviously relevant to the nature of the active species involved in the catalytic polymerization of alkenes; the action of $AlEt_3$ on Cp_2TiCl_2 has also been shown to yield $Cp_2TiCl_2AlEt_2$ (*56–58*), and in the reaction discussed above this has been separated from (**XVI**) by crystallization (*55*).



(XVI)



(XVII)

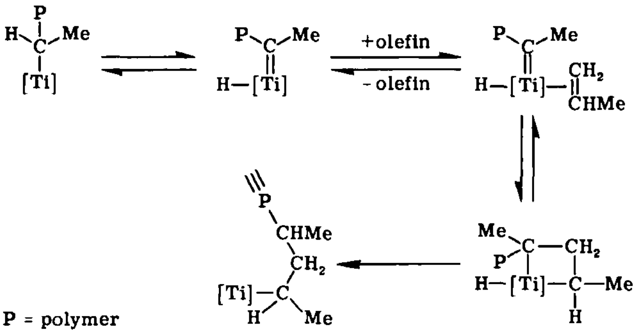
Several studies have been made on reactions involving the interaction of species containing Al–H and Ti–Cl bonds, but so far the precise nature of the products of such reactions has not been defined. The use of ESR spectroscopy to assist in the identification of species such as $Cp_2TiH_2AlH_2$ has already been discussed briefly. A recent investigation, using both calorimetric titrations and ESR methods, has suggested that there are four steps in the $Cp_2TiCl_2/LiAlH_4$ and $CpTiCl_3/LiAlH_4$ reactions. These coincide with Cp_2TiCl_3 or $CpTiCl_3$ to $LiAlH_4$ mole ratios of 2 : 1, 1 : 1, 1 : 1.5, and 1 : 2, as summarized in the accompanying tabulation.

Reactants	Mole ratio	Products
$Cp_2TiCl_2/LiAlH_4$	2 : 1	$Cp_2TiH_2AlCl_2 \cdot Cp_2TiCl$
$CpTiCl_3/LiAlH_4$	2 : 1	$Cp(Cl)TiH_2AlCl_2 \cdot CpTiCl_2$
$Cp_2TiCl_2/LiAlH_4$	1 : 1	$[Cp_2TiH_2Al(H)Cl]_2$
$CpTiCl_3/LiAlH_4$	1 : 1	$[Cp(Cl)TiH_2Al(H)Cl]_2$
$Cp_2TiCl_2/LiAlH_4$	1 : 1.5	$[(Cp_2TiH_2)_2Al_2H_3Cl]$
$CpTiCl_3/LiAlH_4$	1 : 1.5	$[(Cp(Cl)TiH_2)_2Al_2H_3Cl]$
$Cp_2TiCl_2/LiAlH_4$	1 : 2	$Cp_2TiH_2AlH_2 \cdot AlH_3$
$CpTiCl_3/LiAlH_4$	1 : 2	$Cp(Cl)TiH_2AlH_2 \cdot AlH_3$

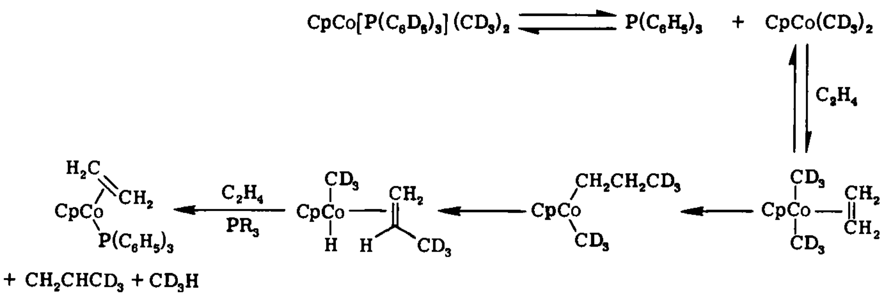
The product formulas are those suggested from both the stoichiometry and the ESR spectra. Thus in the 2 : 1 reaction, the latter technique suggests that both $Cp_2TiH_2AlCl_2$ and Cp_2TiCl are present, presumably in some trinuclear product (*59*). The presence of Ti–H bonds may be inferred in various solutions of titanium chlorides ($TiCl_4$, Cp_2TiCl_2, etc.) with various metal hydrides, where such solutions are used as catalysts for the hydrogenation (and related reactions) of alkenes (*60–63*).

4. *Catalytic and Other Properties of* Ti–H *Bonds*

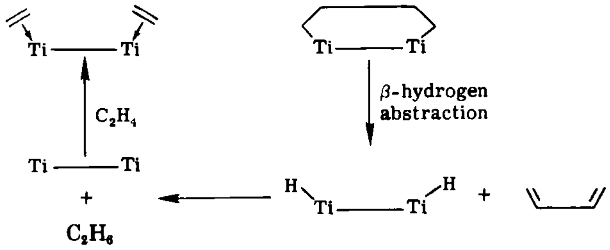
The use of both $TiCl_4/LiAlH_4$ and $TiCl_3/LiAlH_4$ mixtures in organic synthesis has been reviewed (*64, 65*). In addition to the hydrogenation reaction, such mixtures are also active catalysts for the isomerization (*66*) and hydrometallation (*67, 68*) of alkenes, although in the latter case aluminum is invariably the metal that becomes attached to the olefinic bond. The relationship between hydrogenation and isomerization, as well as between metathesis and oligomerization leading to polymerization, has been often emphasized. An original proposal, combining both metallocycles and the elimination of α-hydrogen from metal alkyls believed to be involved in metathesis and isomerization reactions respectively, has been put forward to give a mechanism for the homogeneous and heterogeneous transition-metal-catalyzed polymerization of alkenes. In particular for Ziegler–Natta systems, the Ti-alkyl and Ti–H systems are combined as follows (*69*):



The involvement of the α-elimination reaction in this cycle has been in question following experiments on cyclopentadienyl cobalt complexes, where evidence for olefin insertion for Ziegler–Natta polymerization catalysis has been obtained by labelling experiments, using C_2H_4 with a deuterated cobalt complex (*70*):

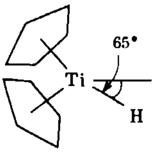


Other studies have shown that both the fulvalene titanocene (V), and the cyclopentadiene dititanium compound (VIII) act as homogeneous catalysts for the conversion of ethylene into ethane and buta-1,3-diene. In this case, an intermediate containing Ti–H bonds has also been proposed (*71*).

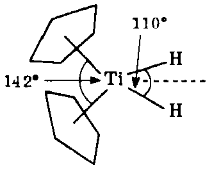


Polymer-attached Cp_2TiCl_2 has been reduced by sodium naphthalide, and the resultant species, which may contain a mixture of Ti(IV), Ti(III), and Ti(II), are more active hydrogenation catalysts for olefins than is the unsupported Cp_2TiCl_2 (*72*). Although distinct Ti–H-containing species were not identified, it has been suggested that the complete reaction occurs at one metal center, in contrast to earlier suggestions that such reductions involve a bimolecular reaction of an intermediate titanocene alkyl and a titanocene hydride (*30*).

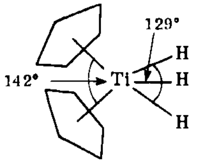
Various experiments have suggested that, in general, hydride derivatives of the group IVA metals show considerable hydridic character as $M^+–H^-$. Thus compounds such as $(Cp_2TiH_2)^-$ and Cp_2TiBH_4 react rapidly with acids liberating hydrogen (*14, 73, 74*), and Cp_2TiBH_4 does not react with amines to liberate BH_3, also consistent with considerable hydridic character of the BH_4 group (*73*). The reaction of hydride compounds of group IVA, VA, and VIA elements with ketones has been used to assess the relative degree of hydridic character in the M–H bond, and although the nature of the other ligands present is important, there does appear to be a decrease in hydridic character on going from group IVA to VIA (*75*). Relatively few theoretical studies have been made on Ti–H bonds, but calculations on the unknown species TiF_3H suggest that the hydrogen atom would be hydridic in nature (*76*). Other calculations have been concerned with the change in stereochemistry through the series TiH_4, TiH_3^+, TiH_3, TiH_3^-, in comparison with their carbon and silicon analogs (*77*), and have dealt with the transannular ligand superhyperfine splittings in the ESR spectra of species such as $Cl_2TiH_2MX_{0-2}$ (M = Li, Mg, Al; X = H, Cl), where the interaction is primarily through space between the titanium d and transannular atom s orbitals (*78*). A comprehensive study of bis(cyclopentadienyl) metal compounds has included calculations for the bent systems Cp_2TiH^+, Cp_2TiH_2, and $Cp_2TiH_3^-$ compounds using the models shown below. In each case, the hydrogen atoms lie in the *yz* plane, which bisects the two Cp rings and contains the twofold rotation axis of the bent Cp_2Ti system. The hydrogen in Cp_2TiH^+ lies off the twofold axis, and the angles between the hydrogen atoms in the bishydride and trishydride compounds are calculated as shown. Although calculations were not carried out for the d^1 complex Cp_2TiH, it was predicted that for the related alkyl compound Cp_2TiR the alkyl group would also lie off the C_2 axis (*79*).



Cp_2TiH^+



Cp_2TiH_2



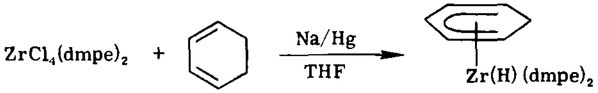
$Cp_2TiH_3^-$

The properties of the various titanium hydride compounds are summarized in Table I.

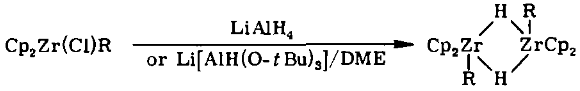
B. ZIRCONIUM HYDRIDE COMPOUNDS

The use of zirconium hydride derivatives in organic synthesis (*80*) and as reagents for coordinating dinitrogen and hydrogenating ligated CO (*81, 82*) has been reviewed, and are therefore not discussed in detail here. The compounds used in these studies are usually derivatives containing either the (Cp_2Zr) or [$(C_5Me_5)_2Zr$] group, e.g., $Cp_2Zr(H)Cl$ or $Cp^*_2ZrH_2$, and the properties of these and related compounds are included in the general summary given next. The monohydrides are discussed first, followed by the dihydride compounds.

a. [$HZr(dmpe)_2(\eta^5\text{-}C_6H_7)$]. While reduction of $ZrCl_4(dmpe)_2$ by Cs/benzene or Na/Hg//THF yields intractable products, in the presence of 1,3-cyclohexadiene a red-brown crystalline hydride is formed in 40% yield. The hydride is stable at ambient temperature, but decomposes evolving hydrogen and benzene above 130°C. The Zr–H group could not be detected spectroscopically (infrared and NMR; in the latter it is assumed that the resonance is obscured by the dmpe or cyclohexadienyl proton resonances between τ 4.5–9.3) (*83, 84*).



b. [$Cp_2Zr(H)R]_2$ *and* [$Cp^*_2Zr(H)R$]. Two independent reports (*84, 85*) have shown that the cyclopentadienyl compounds may be prepared from the corresponding chloro derivative:



where R = (cyclohexyl)methyl, cyclohexyl, ethyl, *n*-octyl, neopentyl (*85*), or $CH(SiMe_3)_2$ (*86*). These compounds all appear to be essentially dimeric in benzene solution, in contrast to the methyl derivative (R = Me), which is reported to be polymeric (*87, 88*). The silyl group conveys a higher stability on the hydride, since the ordinary alkyl compounds are only stable below −30°C in solution. This general instability of hydridoalkyl compounds compared with the corresponding dihydro or dialkyl compounds has been recognized (*89*), and continues into the pentamethylcyclopentadienyl analogs. Thus $Cp^*_2Zr(H)(CH_2CHMe_2)$, prepared from the action of isobutylene on the hydride $Cp^*_2ZrH_2$ (*90*), decomposes slowly at 75°C evolving isobutane, while $Cp^*_2ZrH_2$ and $Cp^*_2ZrMe_2$ are stable over long periods at 100°C (*91*). The Cp* groups also cause the hydridoalkyl to be monomeric.

Both the Cp and Cp* hydridoalkyl compounds react with hydrogen, but different mechanisms have been proposed. In both cases there is *no* evidence for the reductive elimination of alkane followed by the oxidative addition of H_2 to the Cp_2Zr or Cp^*_2Zr fragment. In the case of the $Cp_2Zr(H)R$ compounds, reaction with D_2 leads to incorporation of D into the hydride position, and a mechanism involving deuteride abstraction

TABLE I

TITANIUM HYDRIDE COMPOUNDS AND RELATED DERIVATIVES

Compound	Preparation	Properties	^{1}H NMR (τ, M–H)	Infrared (cm^{-1})	Comments	References
Cp_2Ti	$TiCl_2/NaC_5H_5$/THF	Dark-green solid, air-sensitive, diamagnetic. Forms THF adduct, which decomp. to brown solid.			Stable in inert atmosphere, no spec. props. available.	*2*
$(Cp_2Ti)_2$	$Cp_2TiMe_2/H_2/C_6H_{14}$	Dark-green solid, dimeric in soln.	—	No band near 1230 (no Ti–H?)	Probably contains fulvalene–Ti hydride (V).	*3*
$C_{10}H_{10}Ti$	Photolysis, Cp_2TiMe_2, or Cp_2TiPh_2	Black solid, not completely characterized.	Broad resonances 4–5 (Cp?) 0.5–1.5 (?)	Sharp bands at 790, 1010; no bands at 1220–1230		*32, 33*
	Redn. Cp_2TiCl_2 with Na/Hg, $Na-C_{10}H_8$, or Na	Green diamagnetic volatile solids, react $CO \rightarrow Cp_2Ti(CO)_2$, $N_2 \rightarrow (Cp_2Ti)_2N_2$	—	1228 (Ti–H), 1262, 1300	From IR presence of (V) in samples indicated.	*4–9*
	$(Cp_2TiH)_2 \xrightarrow{150°C} (C_{10}H_{10}Ti)_2 + H_2$	Dark-green solid, dimeric in C_6H_6, paramagnetic. Forms green adduct with THF, but turns brown (cf. Ref. *2*).	—	790, 1010. Very weak band near 1230 (not assigned in Ref. *23*).	Shows similarities to $Cp_2(C_5H_4)Ti_2$ (VIII).	*22, 23*
	$(Cp_2TiH)_2 \rightarrow (Cp_2TiH)_x + H_2$ $\downarrow$ $(C_{10}H_{10}Ti)_2 + H_2$	Metastable titanocene. Dark-colored soln. converted to green fulvalene hydride (V) on heating to 100°C. Reacts $CO \rightarrow Cp_2Ti(CO)_2$.	—	790, 1010	Also closely similar to (VIII). Dark form of Cp_2Ti not well characterized. Also obtained via $Cp_2TiMe_2/H_2/C_6H_{14}$/0°C mixture.	*22, 23, 30*

$(Cp_2Ti)_{1-2}$	Cp_2TiCl_2/Na/toluene under argon	Monomer–dimer equilibrium. Unstable at r.t. Reacts $N_2 \rightarrow Cp_2TiN_2TiCp_2$ as dark-blue complex.	—	790, 1010; no band at 1200–1250. UV max. at 486, 640 nm.	From UV appears very similar to (VIII). Lack of band at 1223 cm^{-1} in infrared indicates $(Cp_2TiH)_2(C_{10}H_8)$ (V) not present.	*31*
$(Cp_2TiH_2)^-$	Cp_2TiCl_2 (or Cp_2TiCl)/EtMgCl (or Mg/THF, or Li *i*Pr)	Dark brown in solution, decomp. by H_2O/acids evolving H_2.	ESR shows 1:2:1 triplet (g = 1.992)	—	—	*14, 15, 18*
Cp_2TiH_2M (M' = MgBr, AlH_2, $AlCl_2$)	$(Cp_2TiCl)_2/LiAlH_4$/THF	Obtained in soln. only, not isolated.	Identified from ESR data (see also Refs. *20, 21*)	—	—	*18–21*
$(Cp_2TiH)_x$	(i) Cp_2TiMe_2/hexane soln./H_2/0°C (ii) Decompn. $(Cp_2TiH)_2$ at 25°C.	Green-gray isomer of $(Cp_2TiH)_2$. Both hydrides show similar reactions but $(Cp_2TiH)_x$ insol. in ethereal solvents. Unstable in toluene, forms H_2 + metastable titanocene.	—	Broad band at 1140, tentative assignment to Ti–H–Ti vibration in $(-H-Ti-H-Ti-)_x$. Otherwise similar to $(Cp_2TiH)_2$.	Stable when stored as solid under Ar.	*22, 23, 33*
$(Cp_2TiH)_2$	Cp_2TiMe_2/H_2/low pressure/no solvent	Diamagnetic violet solid, decomp. 150°C *in vacuo* to green "titanocene" solid (see above). With 1,3-pentadiene $\rightarrow Cp_2Ti$(allyl), $B_2H_6 \rightarrow Cp_2TiBH_4$, etc.	—	Broad band at 1450 from Ti(μ-H_2)Ti group.	Cleaved by ligands to give paramagnetic comps. Unstable on storage as solid.	*22*
$(CpTiH)_2(C_{10}H_8)$ (V) green "titanocene"	Various methods (e.g., see above), typically redn. of Cp_2TiCl_2. Probably present in reaction products reported earlier as "titanocene") (see text).	Diamagnetic green solid, soluble in hydrocarbons. Air- and water-reactive, $H_2O \rightarrow (CpTiOH)_2(C_{10}H_8)$	^{13}C: −105 (Cp), −100 to −122 ppm ($C_{10}H_8$), rel. to TMS. (Ref. *29*).	Band at ~1230 from Ti(μ-H_2)Ti group. Compare with above. Other bands near 800 (790 and 810) and 1010. UV bands at 428, 824 nm.	Structure established by X-ray study on bis(hydroxy) compound (Ref. *25*). Parent ion in mass spectrum. Best prepared by action $Na/C_{10}H_8$ on Cp_2TiCl_2.	*24*

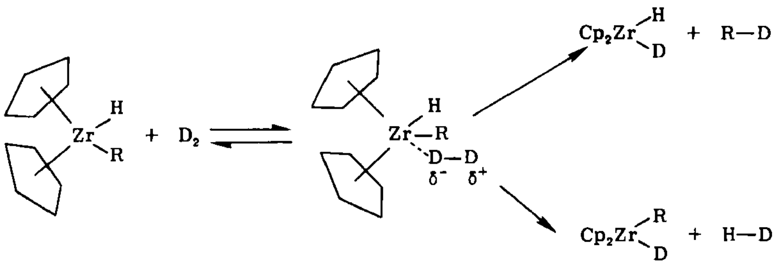
(*table continues*)

TABLE I (Continued)

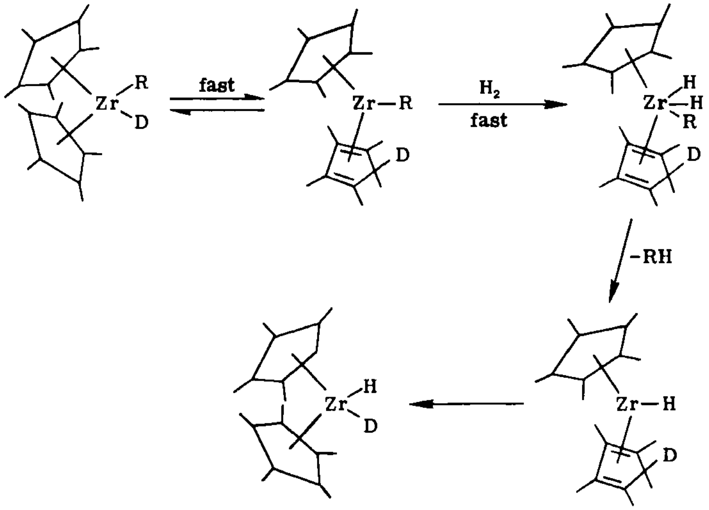
Compound	Preparation	Properties	^{1}H NMR (τ, M–H)	Infrared (cm^{-1})	Comments	References
$Cp_2Ti(C_5H_4)TiCp$ **(VIII)**	Cp_2TiCl_2/K/naphthalene/THF/−80°C	Black, solid, magnetic props. recorded but not reliable. Green soln. in benzene and THF, latter decomp. to brown soln. (cf. Refs. *2, 22, 23*). Reacts H_2, N_2, etc.	Broad resonance at 15 ppm downfield TMS at 32°C—suggests paramagnetic (?). Moves to higher field and broadens on cooling, origin of resonance at $1/T = 0$ is ~7 ppm (cf. Ref. *32* where black titanocene shows Cp protons at 5–6 ppm as broad signal).	Major band at 790, similar to other metallocenes. No splitting of 790 band as there is in **(V)**. Weak band at 1223 cm^{-1} present due to probable presence small amounts of **(V)**.	No significant band at 824 nm in uv, thus only traces of **(V)** present. No evidence of M–H bond apart from trace **(V)**.	*41, 42*
$(CpTi)_2(H)(H_2AlEt_2)(C_{10}H_8)$ **(VII)**	$(CpTiH)_2(C_{10}H_8)/Et_3Al$/toluene/25°C	Reddish-purple crystals, diamagnetic.	4.74 (C_5H_5); 3.55, 5.39, 6.20 ($C_{10}H_8$); 8.63, 8.79, 9.65, 9.87 (CH_2CH_3); 21.62 (TiH_2AlTi); 31.80 (TiHTi).	—	Ti–Ti distance of 3.37Å suggests little bonding, magnetic props. due to exchange in Ti–H–Ti group?	*26*
$[(C_5H_4)TiHAlEt_2]_2(C_{10}H_8)$ **(XVII)**	**(VII)**/Et_3Al/sealed tube/100°C/30 h	Diamagnetic, purple-red solid, m.p. 172–173°C.	1.73, 3.61, 4.16, 5.17, 5.45, 5.75, 5.84 (C_5H_4); 8.47, 8.77, 9.21, 10.00 (CH_2CH_3); 16.59 (TiHAl).	—	Ti–Ti distance 2.91 Å suggests Ti–Ti bond.	*26, 27*
$[Cp(C_5H_4)TiHAlEt_2]_2$ **(XVI)**	Cp_2TiX_2 (X = Ph, Cl, Cl/2)/$AlEt_3$/C_6H_6/70°C/12 h	—	4.92 (Cp); 3.14, 4.17, 5.07, 5.71 (C_5H_4); 8.54, 8.68, 9.36, 9.54 ($AlEt_2$); 17.02 (Ti–H–Al).	—	Separated from $Cp_2TiCl_2AlEt_2$ by crystallization.	*55*

$Cp_2Ti(H)PBu_3$	Cp_2TiCl_2/LiBu/ $H_2/PBu_3/C_6H_5CH_3$ solution	—	—	—	Hydrogenation catalyst.	*47*
$(PhC_5H_3ZnC_5H_4)H$ $TiTiPh(C_{10}H_8)$?	$Cp_2TiPh_2/ZnPh_2/$ Et_2O/60°C/10 h	Diamagnetic, dark-violet solid. Sensitive to H_2O and O_2	—	740, 710 (C_6H_5); 820 (C_5H_5); no band at 1230, thus no TiH_2Ti group.	Interaction of two Ti^{3+} centers proposed to rationalize diamagnetism.	*46*
$[Me_2P(CH_2)_2PMe_2]TiH_3$	Ti(benzyl)$_4$/ ligand/H_2/ 200–400 atm	Polymeric? Black solid.	—	—	—	*49*
$[Ti(OPh)_2]_3H$	$Ti(OPh)_2Cl_2$/2K/Ar atmosphere/toluene/25°C. Under N_2 gives purple N_2 complex.	Gray solid, air-reactive. Magnetic props. suggest one unpaired electron per 3 Ti atoms.	Broad ESR signal, no hyperfine splitting.	1258 (σ-bonded) phenoxo group. No band assigned to Ti–H.	Ti–H detected by reaction with $CCl_4 \rightarrow CHCl_3$.	*50*
$[Ti(OPh)_2Cl(THF)_2]_2H$	$Ti(OPh)_2Cl_2/NaBH_4$/THF	Yellow solid, only stable in THF. Probably dimeric with one unpaired electron per dimer.	—	440 (terminal Ti–Cl), no band from Ti–H.	Ti–H detected as above.	*50*
Cp^*_2Ti	$Cp^*_2TiH_2 \rightleftharpoons Cp^*_2Ti + Cp^*_2TiH$ $\left.\begin{matrix}Cp^*_2Ti\\ Cp^*_2TiH\end{matrix}\right\} \xrightarrow{N_2}$ $(Cp^*_2Ti)_2N_2$ $\downarrow{\scriptstyle vac}$ Cp^*_2Ti	Paramagnetic, yellow-orange, monomeric in benzene. Decomp. to violet $(Cp^*)(C_5Me_4CH_2)$ at r.t.	Broad singlet 86.2 ppm downfield from TMS.	Similar to $Cp^*_2TiCl_2$ from 4000–400. No bands from Ti–H bonds.	Tautomerism between yellow Cp^*_2Ti and green $(Cp^*)(C_5Me_4CH_2)TiH$.	*39*
$Cp^*_2TiH_2$	$(Cp^*)(C_5Me_4CH_2)TiMe$ $+ H_2 \xrightarrow{20°C} Cp^*_2TiH_2$	Diamagnetic orange crystals, monomeric in benzene.	Singlets at δ 1.95 (C_5Me_5) and 0.28 (TiH_2) ppm.	Broad band at 1560, from TiH_2 group.	—	*23, 39*
Cp^*_2TiH	$Cp^*_2TiH_2 \xrightarrow{0.5\ H_2}$ Cp^*_2TiH	Red-brown, crystalline, monomeric in C_6H_6. Unstable evolving H_2.	Broad singlet at 22.2 ppm (30°C). Shows Curie dependence.	Band at 1575 assigned to Ti–H.	—	*39*
$Cp^*(C_5Me_4CH_2)TiH$ (green form of Cp^*_2Ti)	Present in soln. of Cp^*_2Ti. Yellow solns. of Cp^*_2Ti at low temps. change to yellow-green on warming.	Exists in eqilibrium with Cp^*_2Ti at 25°C.	Shows sharp singlets at 7.82, 8.2, 8.38, 8.64, 8.92. No Ti–H resonance detected.	—	—	*39*

from D_2, followed by electrophilic attack of the residual D^+, was proposed (*85*):



The reverse reaction was shown to be faster than the forward one, leading to the incorporation of deuterium into the alkyl hydride. With $Cp_2^*Zr(H)R$, however, no exchange of deuterium with the hydride position occurred with D_2, and the first step was proposed to be a facile and reversible metal-to-ring hydrogen transfer. This was then followed by oxidative addition of H_2 to the intermediate 14-electron system followed by elimination of the hydrocarbon (*91*):

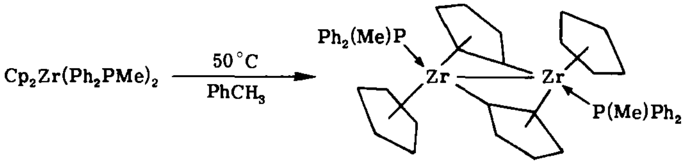


These two pathways have been discussed more recently, and an interesting alternative proposal has been made wherein the formation of an adduct between H_2 and $(C_5R_5)_2ZrR^1_2$ (R,R^1 = H or Me) is proposed. This model utilizes back-bonding from high-energy Zr–R^1 bonding orbitals into the σ^* H_2 orbitals, and is seen as being analogous to the formation of a CO adduct. The model is supported by extended Hückel molecular orbital calculations, and the transition state is suggested to contain an (H--H--H) moiety as a three-center ligand with bonding properties similar to those of an alkyl group. The term *direct hydrogen transfer* has been used to describe this process, and it offers an attractive alternative mechanism for reactions where dihydrogen is activated at a metal center (*92*).

A continuation of the studies on $Cp_2Zr(H)R$ compounds has shown that in addition to hydrogen various tertiary phosphine ligands can also produce reductive elimination of alkane:

$$Cp_2Zr(H)R + 2L \rightarrow Cp_2ZrL_2 + RH$$

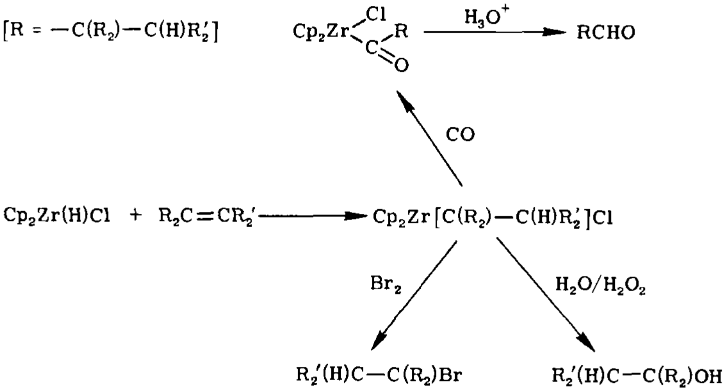
where L = Ph_2PMe, $PhPMe_2$, $Ph_2P(CH_2)_2PPh_2$, and $Me_2P(CH_2)_2PMe_2$, and R = cyclohexylmethyl. The compound $Cp_2Zr[Me_2P(CH_2)_2PMe_2]$ is stable at room temperature, and is a black-green crystalline solid which is sensitive to both air and moisture. The compounds with Ph_2PMe and $PhPMe_2$ decompose slowly at room temperature in solution, affording deep-red diamagnetic dimeric species, as in (*93*).



c. $Cp_2Zr(H)Cl$ *and* $Cp_2Zr(H)AlH_4$. Addition of $LiAlH_4$, LiAl(O-*t*-Bu)$_3$H (*87, 88*) or $NaAl(CH_3OCH_2CH_2O)_2H_2$ (*94*) to Cp_2ZrCl_2 in THF precipitates the hydride $Cp_2Zr(H)Cl$ in high yield. Further details of this preparation and that of Cp_2ZrH_2 have been published (*95*). The infrared spectrum of $Cp_2Zr(H)Cl$ indicates the presence of bridging hydrogens in Zr–H–Zr bonds and is consistent with the formulation of the solid as a polymer. Addition of a further mole of $LiAlH_4$ to $Cp_2Zr(H)Cl$ suspended in THF yields a clear solution, from which $Cp_2Zr(H)AlH_4$ may be obtained. This compound is also polymeric and liberates hydrogen on heating in solvents at 60°C, with the formation of a deep-red diamagnetic product that has yet to be fully characterized (*87, 88*). This contrasts with the properties of the related $Cp_2Zr(H)BH_4$, which is volatile at 60°C and reacts further with amine ligand to yield polymeric Cp_2ZrH_2 (*73*).

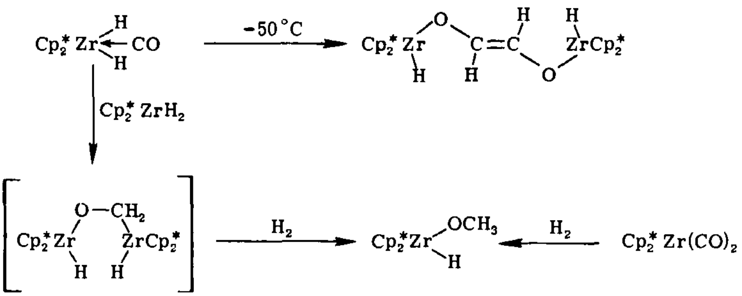
$$\begin{array}{lll} Cp_2Zr(BH_4)_2 \xrightarrow{NMe_3} & Cp_2Zr(H)BH_4 \xrightarrow{NMe_3} & (Cp_2ZrH_2)_x \\ & + BH_3 \cdot NMe_3 & + BH_3 \cdot NMe_3 \end{array}$$

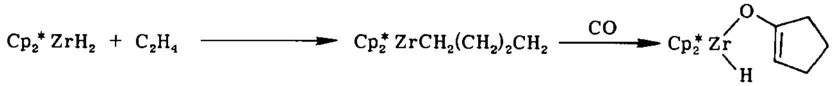
The use of $Cp_2Zr(H)Cl$ in hydrozirconation reactions has been referred to (*80*), and consists of addition to the Zr–H moiety to unsaturated organic molecules, frequently alkenes and alkynes (*96*). The resulting alkyls, or alkenyls, undergo further reactions—e.g., electrophilic halogenation, oxidation, or insertion reactions (*97*)—to yield a range of organic products, as in



The use of $Cp_2Zr(Cl)BH_4$ [prepared by the action of $BH_3 \cdot Me_2S$ on $Cp_2Zr(H)Cl$ (*98*) or by treating Cp_2ZrCl_2 with 1 mole equivalent of $LiBH_4$ (*73*)] as a selective reducing agent for converting aldehydes or ketones to alcohols has also been recently exploited (*98*).

d. $Cp_2^*Zr(H)OR$ (R = Me, cyclo-C_5H_7, $CH{=}CHCHCMe_2$) *and* $(Cp_2^*ZRH)_2(\mu\text{-}OCH{=}CHO)$. A series of monohydrides has been obtained by insertion into one of the Zr–H bonds of the pentamethylcyclopentadienyl compound, $Cp_2^*ZrH_2$ (*90, 99*):



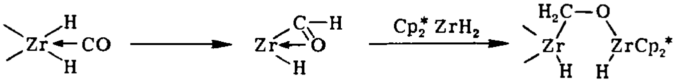


$$Cp_2^*ZrH_2 + H_2C{=}CMe_2 \longrightarrow Cp_2^*Zr(H)CH_2CHMe_2 \xrightarrow{CO} Cp_2^*Zr(H)(OCH{=}CHCHMe_2)$$

If the last reaction of the alkyl hydride with CO is carried out at −50°C, an acyl intermediate $Cp_2^*Z(H)(Me_2CHCH_2CO)$ is formed and has been identified from its ^1H-NMR spectrum. Rearrangement to the final product $Cp_2^*Zr(H)(OCH{=}CHCH\ Me_2)$ occurs at −20°C.

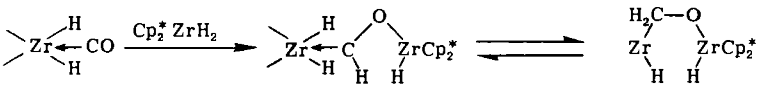
The question of the mechanism of the insertion of the CO into the Zr–H bond remains to be solved, and different mechanisms may operate. Two routes appear the most likely:

1. Formation of a formyl intermediate by migration of CO into a Zr–H bond and reduction of this by $Cp_2^*ZrH_2$.

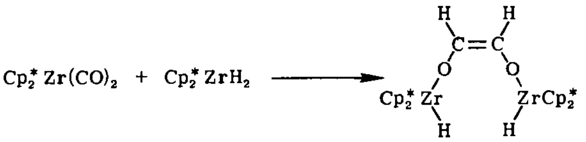


This appears to be favored by the reaction involving isonitriles given in Section I,B,e.

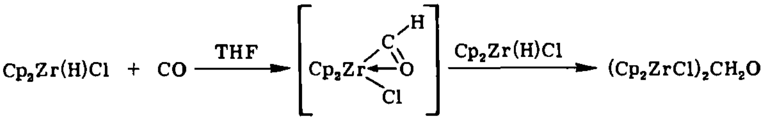
2. Direct reduction, by attack on the coordinated CO.



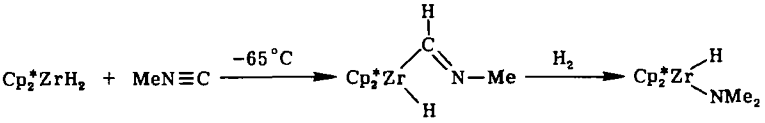
Support for this path comes from the reaction between $Cp_2^*Zr(CO)_2$ and $Cp_2^*ZrH_2$, which forms a *cis*-enediolate.



Carbonyl insertion into the Zr–H bond of $Cp_2Zr(H)Cl$ also occurs, yielding the monomeric $[Cp_2Zr(H)Cl]_2CH_2O$, and this has also been suggested to proceed through reduction of a formyl intermediate as in (1) by a further mole of $Cp_2Zr(H)Cl$ (*100*).

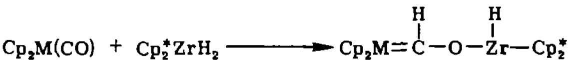


e. $Cp^*_2Zr(H)CH{=}NMe$ *and* $Cp^*_2Zr(H)NMe_2$. The addition of isonitriles to $Cp^*_2ZrH_2$ affords first an intermediate formimidoyl hydride species—e.g., $Cp^*_2Zr(H)(CH{=}NMe)$—that is generally unstable at room temperature but reacts further with hydrogen forming a stable hydride:

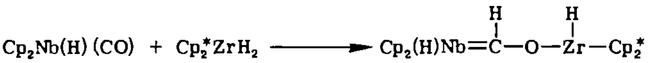


This sequence provides support for the migratory insertion of the incoming ligand (e.g., MeNC, and by inference, CO) into the Zr–H bond as outlined in mechanism (1) in Section I,B,e above (*101*).

f. $Cp^*_2Zr(H)OCH{=}MCp_2$ (M = Mo, W), $Cp^*_2Zr(H)OCH{=}Nb(H)Cp_2$, *and* $Cp^*_2Zr(H)OCH_2Nb(CO)Cp_2$. The possibility that $Cp^*_2ZrH_2$ might act as a hydride transfer reagent has been realized in reactions where CO is coordinated to another transition metal. Thus, with $Cp_2M(CO)$ (M = Cr, Mo, or W) and $Cp_2Nb(H)CO$, the bimetal species are obtained,



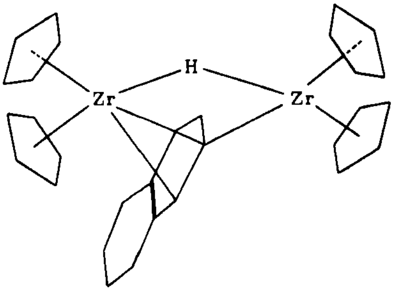
$$Cp_2M(CO) + Cp^*_2ZrH_2 \longrightarrow Cp_2M{=}\overset{H}{\overset{|}{C}}{-}O{-}\overset{H}{\overset{|}{Zr}}{-}Cp^*_2$$



$$Cp_2Nb(H)(CO) + Cp^*_2ZrH_2 \longrightarrow Cp_2(H)Nb{=}\overset{H}{\overset{|}{C}}{-}O{-}\overset{H}{\overset{|}{Zr}}{-}Cp^*_2$$

with the identity of the tungsten derivative being established uniquely by X-ray diffraction, and the W–C bond distance being short, 2.005(13) Å, as expected (*102*). Unpublished observations have shown that several transition-metal carbonyl compounds react with $Cp^*_2ZrH_2$, but only with those containing a single M–CO group are the zirconoxycarbenes, shown above, obtained (*82*).

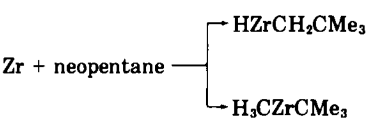
g. $Cp_2Zr(C_{10}H_7)(H)ZrCp_2$. The isolation of μ-($\eta^1:\eta^5$—C_5H_4)η-C_5H_5)$_3$ Ti_2 (**VII**) from the low-temperature reduction of Cp_2TiCl_2 with potassium naphthalene has been discussed (*41*); a similar reduction of Cp_2ZrCl_2 has yielded a dark green compound. Although this showed no obvious absorptions due to M–H bonds in its infrared spectrum, a singlet at δ_{SiMe_4} −9.3 in its ^{1}H-NMR spectrum and reactions with HCl and CH_3I indicated that it was a hydride derivative. The structure (**XVIII**) from X-ray diffraction showed a naphthyl ligand bridging two metal atoms, and the hydride, which was not detected from the X-ray data, was also assumed to be in a bridging position (*103*).



(XVIII)

While (**XVIII**) is stable in the solid state, it decomposes slowly in solution, turning blue or purple, to produce other zirconium hydride species that have yet to be characterized.

h. $HZrCH_2CH_2CMe_3$. Reaction of Zr atoms with alkanes (e.g., isobutane, neopentane) condensed into a matrix at 77 K results in oxidative addition of the metal to both C–C and C–H bonds. In the latter case, the presence of a black solid hydride has been inferred from hydrolysis reactions and deuteration studies (e.g., *104*).



i. $Cp(C_5H_4)ZrH$. Although this compound has not been isolated, it has been postulated, from ESR spectra, as an intermediate in the photolysis of Cp_2ZrMe_2. The compound is photolabile and degrades further by cleavage of the Zr–H bond to form the Zr(II) derivative (*105*).

$$Cp_2ZrMe_2 \xrightarrow{h\nu} Cp_2Zr(III)Me + Me\cdot \rightleftharpoons (Cp_2ZrMe)_2 \underset{h\nu}{\overset{\Delta}{\rightleftharpoons}} Cp_2Zr + Cp_2ZrMe_3$$

$$Cp_2Zr \xrightarrow{\Delta} Cp(C_5H_4)Zr(III)H \xrightarrow{h\nu} [Cp(C_5H_4)Zr]_n + H\cdot$$

1. Dihydride Compounds

a. Cp_2ZrH_2 *and* $(C_5H_4R)_2ZrH_2$. The white polymeric hydride $(Cp_2ZrH_2)_x$ was first reported in 1967, and may be prepared by three methods, two of which are (*73, 87, 88*)

$$Cp_2Zr(BH_4)_2 \xrightarrow{2NMe_3} (Cp_2ZrH_2)_x + 2BH_3 \cdot NMe_3$$

$$(Cp_2ZrCl)_2O + LiAlH_4 \xrightarrow{THF} (CpZrH_2)_x + LiCl + (AlOCl)_2$$

The $LiAlH_4$ may be replaced by four moles of $LiAl(O\text{-}t\text{-}Bu)_3H$, but when only two moles of the latter are used, the hydride precipitates as $(Cp_2ZrH)_2O(Cp_2ZrH_2)$ (*88*). The $(Cp_2ZrH_2)_x$ acts as a catalyst for the hydrogenation of alkenes and alkynes (*106*).

The third preparative route consists of the hydrogenolysis of M–C bonds in the reaction (*107*)

$$(\eta^5\text{-}C_5H_4R)_2MCl_2 \xrightarrow[-20^\circ C]{MeLi} (\eta^5\text{-}C_5H_4R)M(CH_3)_2 \xrightarrow[80^\circ C]{H_2,\ 60\ atm} (\eta^5\text{-}C_5H_4R)_2MH_2$$

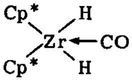
where R = H, Me, Me_2CH, Me_3C, $PhCH_2$, or Ph(Me)CH (two stereoisomers), and M = Zr or Hf. This method has been used to prepare an optically active dimethyl compound $(C_5H_5)[C_5H_4CH(Me)Ph]ZrMe_2$, although when this was used to hydrogenate alkenes under hydrogen pressure the products showed no induced optical activity, probably due to the distance of the chiral center from the catalytic center.

b. $(C_5Me_5)_2ZrH_2$ *and the adducts* $(C_5Me_5)_2ZrH_2 \cdot L$ (L = CO, PF_3). While $Cp_2^*ZrH_2$ may be obtained from $Cp_2^*ZrCl_2$ by treatment with $Li(BEt_3H)$ or $Na[AlH_2(OCH_2CH_2OCH_3)_2]$, it is better prepared from the nitrogen derivative (*81, 82, 90, 99*).

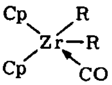
$$2Cp_2^*ZrCl_2 \xrightarrow[N_2]{Na/Hg} [Cp_2^*ZrN_2]_2N_2 + 4NaCl$$

$$[Cp_2^*ZrN_2]_2N_2 + 2H_2 \xrightarrow[PhCH_3]{0^\circ C} 2Cp_2^*ZrH_2 + 3N_2$$

Unlike the polymeric $(Cp_2ZrH_2)_x$, this pale yellow compound is soluble in hydrocarbons and is monomeric. Since it is a 16-electron compound, it not unexpectedly forms adducts; however, the somewhat surprising feature is that it forms only $Cp_2^*ZrH_2 \cdot L$ (where L = CO or PF_3; only stable below room temperature), and does not combine with other ligands such as $P(OMe)_3$, PPh_3, or PMe_3. The precise structure of these adducts remains uncertain. Although they are usually depicted as possessing a symmetrical structure (**XIX**), in a recent study where CO coordinates to $Cp_2Zr(C_6H_5)_2$ the resulting η^3-benzoyl compound has its carbonyl oxygen in the lateral position, indicating the initial formation of an unsymmetrical adduct (**XX**) (*108*).



(XIX)



(XX)

The hydridic nature of the hydrogen atoms in $Cp^*_2ZrH_2$ has been emphasized (*75*), and the $Zr^+{-}H^-$ character of the bond is illustrated by reactions with HCl, CH_3I, and CH_2O (*81*), as in

$$Cp^*_2ZrH_2 + 2HCl \xrightarrow{-80°C} Cp^*_2ZrCl_2 + 2H_2$$

$$Cp^*_2ZrH_2 + 2CH_3I \longrightarrow Cp^*_2ZrI_2 + 2CH_4$$

c. H_2Zr(tetrahydroindenyl)$_2$ *and* H_2Zr(COT). Hydrogenation (H_2, 80 atm, 140°C/8 h) of (π-indenyl)$_2ZrMe_2$ affords the tetrahydroindenyl hydride derivative $(C_9H_{13})_2ZrH_2$, which is soluble in aromatic hydrocarbons and dimeric in benzene. The ^{1}H-NMR spectrum of the dimer indicates that there are two sets of hydride hydrogens that are exchanging at 30°C, but not at −36°C, and that within the two sets, each of the two hydrogens are magnetically equivalent. It has therefore been suggested that at least one set occupies bridging positions between two zirconium atoms (*109*).

The reduction of $Zr(OR)_4$ compounds with Et_2AlH in the presence of cyclooctatetraene (COT) produces the dihydride $(COT)ZrH_2$. This reacts with protonic hydrogens, liberating hydrogen; but since the dihydrides in general act as efficient hydrogenating catalysts for alkenes, the final hydrocarbon product formed is essentially a mixture of cyclooctatriene and cyclooctadiene (*110*), e.g.,

$$\begin{tikzcd}
(COT)ZrH_2 \arrow[r, "2EtOH"] & C_8H_{12} + Zr(OEt)_2 \arrow[r, "\frac{1}{2}O_2"] \arrow[d, "2EtOH"] & OZr(OR)_2 \\
& H_2 + Zr(OEt)_4 &
\end{tikzcd}$$

Different products may be obtained from the initial reaction; thus when tetraallylzirconium is treated with COT and Et_2AlH, the 1 : 1 and 1 : 2 adducts $(COT)_2Zr(HAlEt_2)_{1\text{ or }2}$ are formed. In addition, the complex $(COT)_2Zr \cdot (HAlEt_2)_2$ may be formed in the reaction shown below, and it is postulated to ionize in toluene solution to form an anion containing a Zr–H–Al bridge bond (*110*).

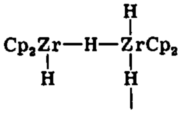
$$\mathrm{Zr(OR)_4 + 4AlEt_3 + 2COT \rightarrow (COT)_2Zr + 4Et_2AlOR + [4C_2H_5]}$$

$$\begin{array}{l} \mathrm{(COT)_2Zr + 2Et_2AlH \rightarrow (COT)_2Zr \cdot (HAlEt_2)} \\ \qquad\qquad\qquad\qquad\qquad\quad \upharpoonleft\!\downharpoonright \\ \qquad\qquad\qquad\qquad\quad \mathrm{[(COT)_2ZrH(Et_2)AlH]^- + [Et_2Al]^+} \end{array}$$

d. $H_3Zr(dmpe)_2$. This compound has been referred to in the section on titanium, and is prepared by reacting zirconium tetraphenyl with hydrogen under high pressure in the presence of the ligand $Me_2P(CH_2)_2PMe_2$(dmpe) (*49*).

2. *Spectroscopic Properties of Zirconium Hydrides*

These are summarized in Table II. The Zr–H stretching frequency now appears to lie in the region 1600–1500 cm^{-1}, rather than 2000–1800 cm^{-1} as observed for the group VI–VIII transition-metal hydrides (*81*). Frequencies for ν(M–H) have been observed at 1710 cm^{-1} and 1735 cm^{-1} for Cp_2NbH_3 (*111*) and Cp_2TaH_3 (*112*), respectively, and main group hydrides (e.g., Ge, Sn, Pb) show similar absorptions near 2000 cm^{-1} (*113*). Some uncertainty still exists since bridging hydride vibrational modes (e.g., Zr–H–Zr) have not been positively identified. Thus $(Cp_2ZrH_2)_x$ shows broad absorptions associated with Zr–H vibrations at 1540–1520 cm^{-1} and ~1300 cm^{-1} (*73*, *87*); assuming a polymeric structure of the general type



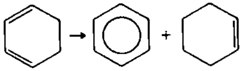
$$\begin{array}{ccc} & & \mathrm{H} \\ & & | \\ \mathrm{Cp_2Zr} & \mathrm{—H—} & \mathrm{ZrCp_2} \\ | & & | \\ \mathrm{H} & & \mathrm{H} \\ & & | \end{array}$$

would suggest that the terminal and bridging vibrations should be assigned to the bands at ~1500 cm^{-1} and ~1300 cm^{-1}, respectively. The polymeric $Cp_2Zr(H)Cl$ shows only one ν(Zr–H) absorption at 1390 cm^{-1}, presumably arising from a bridging Zr–H–Zr bond (*87*).

In the ^{1}H-NMR spectra of zirconium hydride compounds, the unusual feature compared with later transition-metal hydrides is the low-field chemical shift of the hydride hydrogen. For $Cp_2^*ZrH_2$, δ_{Zr-H} is 7.46 (*90*); a weak resonance signal at δ 4.5 has been tentatively assigned to the simple hydride hydrogen in $Cp_2Zr(H)BH_4$ (*73*); and similar signals for $Cp_2^*TiH_2$ and $Cp_2^*HfH_2$ have been observed at δ 0.28 and 15.6, respectively (*81*, *90*). A more comprehensive listing of the hydride shifts for many of the compounds discussed above has been given, and all the

TABLE II

ZIRCONIUM HYDRIDE COMPOUNDS

Compound	Preparation	Properties	¹H NMR (τ, M–H)	Infrared (cm^{-1})	Comments	References
(η^5-C_8H_7)Zr(H)(dmpe)$_2$	$ZrCl_4$(dmpe)$_2$/ Na/Hg/THF	Red-brown crystals, decomp. above 130°C evolving H_2. Reacts HCl → H_2 (from Zr–H).	Zr–H not detected, C_8H_7 ligand from 2.59–5.5	Zr–H not detected (parent ion found in mass spectrum).	Catalyst for disproportionation 	*83, 84*
[Cp_2Zr(H)R]$_2$[R = alkyl, cyclohexyl, CH(SiMe$_3$)$_2$]	Cp_2Zr(Cl)R/LiAlH$_4$ or Li[AlH(O-*t*Bu)$_3$]/ DME	Colorless solids, dimeric in benzene except R = Me (polymeric). Generally unstable at r.t. except silyl derivative.	~12 (Zr–H)	1500 and 1310 in [Cp_2Zr(H)Me]$_n$ from Zr–H–Zr	—	*85, 86*
Cp_2Zr(H)Cl	Cp_2ZrCl_2/LiAlH$_4$/THF	Polymeric white solid, –Zr–H–Zr–bonds. Reacts alkenes, alkynes, etc.	Insolubility limits investigation (Ref. *88*).	1390 (Zr–H–Zr)	Further addn. LiAlH$_4$ gives Cp_2Zr(H)AlH$_4$, also probably polymeric.	*87, 88, 94, 95*
Cp_2Zr(H)BH$_4$	Cp_2Zr(BH$_4$)$_2$/1 mol NMe$_3$	Volatile white solid, hydrolyzed in air releasing hydrogen.	5.47 (Zr–H?); 4.30 (Cp); 10.20 (BH$_4$).	1623 (Zr–H); 2400, 1945, 1132 (BH$_4$).	—	*73*
Cp_2Zr(H)($C_{10}H_7$)ZrCp_2 **(XVIII)**	Cp_2ZrCl_2/K/$C_{10}H_8$/ THF/–80°C	Dark-green solid. Decomposes in soln., reacts MeI → CH$_4$. No magnetic data.	19.3 (Zr–H); 4.0 (Cp); 2–5 ($C_{10}H_7$).	No Zr–H band detected, strong band at ~800 from Cp groups.	Structure from X-ray data, H in Zr–H bond not located.	*103*
Zr(H)(CH$_2$CMe$_3$)	Zr atoms/isobutane/ condense in matrix at 77 K	Black solid, not fully characterized, Zr–H bond deduced from hydrolysis.	—	Unstable on warming from matrix temp. No spectroscopic data.	Oxidative addition of C–H bond to metal atom.	*104*
(Cp_2ZrH_2)$_x$	Cp_2Zr(BH$_4$)$_2$/2 mol NMe$_3$ or [Cp_2ZrCl]$_2$O/ LiAlH$_4$/THF/25°C	White polymeric solid.	—	1520 and 1300 (Zr–H–Zr).	Hydrogenation catalyst.	*73, 87, 88, 95*

(*table continues*)

TABLE II (Continued)

Compound	Preparation	Properties	^{1}H NMR (τ, M–H)	Infrared (cm^{-1})	Comments	References
$[(C_5H_4R)_2ZrH_2]_x$ (R = Me, Me_2CH, etc.)	$(C_5H_4R)_2ZrMe_2/H_2/60$ atm/80°C	White polymeric solids, except where R = Me_3C or Me_2CH when compounds are dimers. Sensitive to air and moisture.	—	—	Hydrogenation catalysts for alkenes and alkynes.	*107*
$[(C_9H_{13})_2ZrH_2]_2$ (C_9H_{13} = tetrahydro-indenyl)	$(C_9H_9)ZrMe_2/H_2/80$ atm/140°C/8 h	Sol. hydrocarbons, dimeric in C_6H_6. D_2 affects exchange in ZrH_2 groups.	5.41, 11.56 (Zr–H).	1545, 1285 (Zr–H–Zr).	Two sets of ZrH_2 protons in dimer are inequivalent in H-NMR spectrum.	*109*
$(COT)ZrH_2$	$Zr(OR_4)/Et_2AlH/COT$	Reacts $H^+ \rightarrow H_2$; $EtOH \rightarrow C_8H_{12} + Zr(OEt)_4 + H_2$.	—	1537, 1310 (Zr–H).	Bridged species, e.g., $(COT)Zr(HAlEt_2)_{1\text{ or }2}$, also prepared.	*110*
$(Cp_2ZrH_2 \cdot AlMe_3)_2$	$(Cp_2ZrH_2)_x/AlMe_3/C_6H_6$	Pale-blue, proposed dimer, unstable r.t. → unidentified crimson comp.	7.08 (Zr–H–Zr); 9.08 (Zr–H–Al); 4.50 (Cp); 10.41 (Al–Me).	1780 (Zr–H–Al); 1350 (Zr–H–Zr).	—	*116*
$Cp_2Zr(\mu\text{-}H)_3Al(i\text{Bu})_2$	$(Cp_2ZrH_2)_x/(i\text{Bu})_2AlH/C_6H_6/25°C$	Deep-blue oil, unstable at r.t.	$\left.\begin{matrix}10.28\\12.03\end{matrix}\right\}$ Zr–H–Al 4.43 (Cp)	—	Reacts $(i\text{Bu})_2AlCl \rightarrow Cp_2Zr(H)(\mu\text{-}H)_2[Al(i\text{Bu})_2]_2Cl$. Also $AlMe_3 \rightarrow Cp_2Zr(H)(\mu\text{-}H)_2[Al(i\text{Bu})_2](AlMe_3)$.	*117*
$(Cp_2ZrH_2)_2[Al(i\text{Bu})_2R]_2$ (R = *neo*hexyl)	$Cp_2ZrR_2/2(i\text{Bu})_2AlH$	Reacts with further $(i\text{Bu})_2AlH \rightarrow$ trihydride $Cp_2Zr(H)(\mu\text{-}H)_2[Al(i\text{Bu})_3][Al(i\text{Bu})R]$.	—	—	Indicates interchange of *neo*hexyl/H groups between Zr and Al.	*117*
$[Cp_2Zr(H)]_2OCp_2ZrH_2$	Cp_2ZrH_2/2 mol $LiAl(O\text{-}t\text{Bu})_3H$/THF	Pale-pink insoluble polymer. Reacts acids, all Zr–H bonds → H_2.	—	1510, 1385, 1240 (Zr–H–Zr)	—	*88*
$(dmpe)_2ZrH_3$	$Zr(benzyl)_4/H_2/dmpe/C_6H_6$/200 atm	Dark-brown solid, reacts HCl → H_2.	—	1280 (Zr–H–Zr)	—	*49*
$Cp^*_2ZrH_2$	$Cp^*_2ZrCl_2/LiBEt_3H$ or $(Cp^*_2ZrN_2)_2N_2/2H_2/PhCH_3$/0°C	Monomeric, pale-yellow solid, sol. hydrocarbons. Forms adducts $Cp^*_2ZrH_2 \cdot L$ (L = CO or PF_3) at low temps.	2.54 (Zr–H); 7.98 (Cp*).	1555 (Zr–H)		*81, 82, 90, 99*

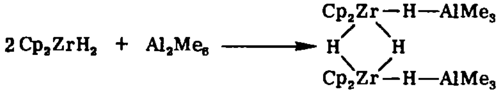
$Cp^*_2Zr(H)(CH_2CHMe_2)$	$Cp^*_2ZrH_2/CH_2{=}CMe_2$ at r.t.	Pale-yellow, monomeric in benzene, stable to 70°C when $CH_2{=}CMe_2$ evolved.	3.57 (Zr–H); 8.07 (Cp*).	—	Deuterated species also prepared.	*90*
$Cp^*_2Zr(H)(OCH_3)$	$CP^*_2Zr(CO)_2/H_2/110°$ or $Cp^*_2ZrH_2(CO)/$ $Cp^*_2ZrH_2/H_2$	White crystals, monomeric, reacts $HCl \rightarrow Cp^*_2ZrCl_2$.	4.3 (Zr–H); 6.13 (OCH_3); 8.04 (Cp*).	1590 (Zr–H); 1140 (C–O).		*90, 99*
$(Cp^*_2ZrH)_2(OCH{=}CHO)$	Allow $Cp^*_2ZrH_2(CO)$ to warm to −50°C.	Yellow crystalline solid, reacts $MeI \rightarrow$ $[Cp^*_2ZrI]_2$ $(OCH{=}CHO)$.	4.27 (Zr–H); 8.06 (Cp*); 3.45 ($OCH{=}CHO$).	1580 (Zr–H); 1205 (C–O).	X-Ray studies on $(Cp^*_2ZrI)_2$ $(OCH{=}CHO)$ in accord with proposed structures for hydride.	*90*
$Cp^*_2Zr(H)$ $(\overline{OC{=}CHCH_2CH_2CH_2})$	$Cp^*_2\overline{Zr{-}CH_2CH_2CH_2}/$ CO/25°C or $Cp^*_2Zr(CO)_2/C_2H_4/h\nu$	White crystalline solid, reacts $MeI \rightarrow CH_4 +$ $Cp^*_2Zr(I)(OC{=}CH$ $CH_2CH_2CH_2)$.	3.93 (Zr–H); 8.03 (Cp*); $\left.\begin{matrix}5.48\\7.5\text{–}8.0\end{matrix}\right\}(C_5H_7O)$.	1538 (Zr–H); 1628 (C=C); 1275 (C—O).	—	*90*
$Cp^*_2Zr(H)(Me_2CHCH_2CO)$	$Cp^*_2Zr(H)(CH_2CHMe_2)$ CO/1 atm/−50°C	Transient acyl intermediate, rearranges at −20°C to $Cp^*_2Zr(H)$ $(OCH{=}CHCHMe_2)$.	6.34 (Zr–H); 8.18 (Cp*); $\left.\begin{matrix}7.46\\8.80\end{matrix}\right\}(C_5H_9O)$.	—	—	*90*
$Cp^*_2Zr(H)$ $(OCH{=}CHCHMe_2)$	Final product of rearrangement at −20°C given above.	Orange oil, but not isolated pure.	3.96 (Zr–H); 8.06 (Cp*); $\left.\begin{matrix}3.37\\5.39\end{matrix}\right\}(C_5H_9O)$.	—	—	*90*
$Cp^*_2Zr(H)NMe_2$	$Cp^*_2ZrH_2/MeNC/H_2/1$ atm/reaction warmed from −80° to 25°C.	Reacts $MeI \rightarrow$ $Cp^*_2Zr(I)NMe_2 + CH_4$.	3.59 (Zr–H); 8.06 (Cp*); 7.59 (NMe_2).	1550 (Zr–H)	Intermediate reaction product is formimidoyl hydride $Cp^*_2Zr(H)$ $C(H){=}NMe$.	*101*
$Cp^*_2Zr(H)(OCH{=}MCp_2)$ (M = Mo or W)	$Cp^*_2ZrH_2/Cp_2M(CO)/$ $C_6H_5CH_3/{-}80°C$	W comp. brown crystalline solid, thermally stable.	4.28 (W comp.); 4.20 (Mo comp.); 4.06 (Cr comp. at −3°C).	1560 (Zr–H, W comp.) 1543 (Zr–H, Mo comp.)	X-Ray structure on tungsten compound. Cr compound decomp. at 25°C.	*102*
$Cp^*_2Zr(H)$ $[OCH{=}Nb(H)Cp_2]$	$Cp^*_2ZrH_2/Cp_2Nb(H)$ $(CO)/{-}80°C$	Product in nearly quantitative yield from NMR.	4.30 (Zr–H); 4.98 (Cp); 8.01 (Cp*); 13.14 (Nb–H); ^{13}C also reported.	1567 (Zr–H); 1701 (Nb–H).	—	*102*
$Cp^*_2Zr(H)$ $[OCH_2Nb(CO)Cp_2]$	$Cp^*_2ZrH_2/Cp_2Nb(H)$ (CO) under CO at 25°C	—	4.77 (Zr–H); 5.28 (Cp); 7.99 (Cp*).	1553 (Zr–H); 1898 (C≡O).	—	*102*

resonances lie in the region δ 0–7.46 (*90*). Although the metal atom in each of these compounds possesses formally a d^0 electron configuration and may therefore be considered to be more like the main-group elements in some of its properties, the reason for the low-field shift remains in doubt at present.

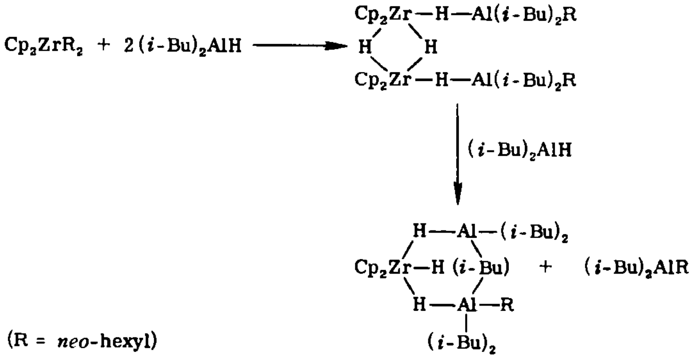
3. Zirconium Hydrides Containing Bridge Bonds Zr–H–M (M = B *or* Al)

This section does not review comprehensively all the tetrahydroborate derivatives, since these have been adequately covered elsewhere (*50*). The aluminohydride compound $Cp_2Zr(H)AlH_4$ has been mentioned, but several similar hydrides have been identified. Such compounds are relevant in particular to known reactions where titanium(IV) or zirconium(IV) compounds catalyze the addition of Al–H bonds to alkenes and alkynes (*114, 115*).

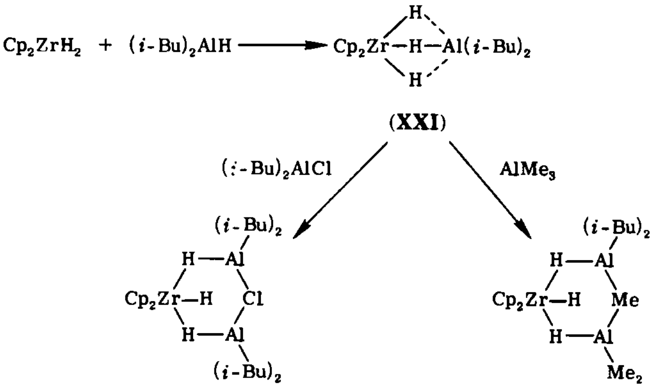
a. $[Cp_2ZrH_2 \cdot AlMe_3]_2$. The addition of $AlMe_3$ to a suspension of $(Cp_2ZrH_2)_x$ in benzene leads to a pale-violet solution from which a pale-blue compound $Cp_2ZrH_2 \cdot AlMe_3$ may be isolated in high yield. This is postulated to be a dimer on the basis of spectroscopic data and is unstable at room temperature, forming an unidentified crimson compound and evolving methane and hydrogen (*116*).



A similar product has been reported to result from the action of $(i\text{-Bu})_2$ AlH on $Cp_2Zr(\textit{neo}\text{-hexyl})_2$, and here alkyl–hydride exchange clearly occurs. Further addition of $(i\text{-Bu})_2AlH$ displaces $(i\text{-Bu})_2Al(\textit{neo}\text{-hexyl})$ and affords the trihydride (*117*):



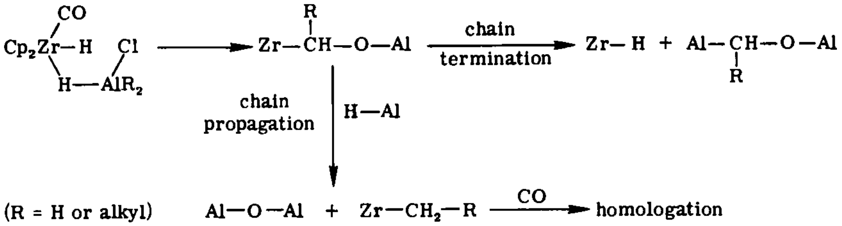
b. $Cp_2ZrH_3AlR_2$, $Cp_2Zr(H)(\mu\text{-}H_2\text{-}Al\text{-}R_2\text{-}R\text{-}AlR'_2)$, *and* $Cp_2Zr(H)[\mu\text{-}H_2\text{-}(AlR_2)\text{-}Cl]$. If Cp_2ZrH_2 reacts with $(i\text{-}Bu)_2$ AlH instead of $AlMe_3$, the deep-blue oily complex (**XXI**) is formed. While this decomposes at room temperature, treatment of (**XXI**) with $(i\text{-}Bu)_2AlCl$ yields the thermally stable compound (**XXII**) as a pale-violet oil. Alternatively, treatment of (**XXI**) with $AlMe_3$ produces the mixed alkyl oily complex (**XXIII**) (*96, 117*).



(**XXI**)

(**XXII**) (**XXIII**)

The compound (**XXII**) is also obtained upon addition of 3 mol $(i\text{-}Bu)_2AlH$ to Cp_2ZrCl_2 in benzene. It is interesting that this compound absorbs 2 mol CO, and the resulting golden-yellow solution on hydrolysis yields a series of alcohols ROH (R = Me, Et, *n*-Pr, *n*-Bu). The mechanism has been postulated to involve the initial dissociation of 1 mol $(i\text{-}Bu)_2AlH$, followed by coordination of CO to zirconium; subsequent chain propagation occurs as shown below (*118*).



The properties of the various zirconium hydride compounds are summarized in Table II.

C. Hafnium Hydride Compounds

In contrast to the extensive zirconium series, there have been relatively few hafnium hydride compounds reported (Table III). The

TABLE III

HAFNIUM HYDRIDE COMPOUNDS

Compound	Preparation	Properties	^{1}H NMR (τ, M–H)	Infrared (cm^{-1})	Comments	References
$Cp_2Hf(H)Cl$	$Cp_2HfCl_2/LiAlH_4$	White solid, reacts alkenes, appears similar to Zr analog.	—	—	—	*119*
$(Cp_2HfH_2)_x$	Cp_2HfMe_2/H_2	White insoluble polymeric solid.	—	—	Methyl comp. from Cp_2HfCl_2/LiMe/−20°C.	*107*
$[(C_5H_4R)_2HfH_2]_x$ (R = Me, $PhCH_2$, PhCHMe, Me_3C, Me_2CH)	Cp_2HfMe_2/H_2/ 60 atm/80°C	For R = Me_3C, Me_2CH, $x = 2$, sol. hydrocarbons. For R = Me, $PhCH_2$, PhCHMe, polymers, insol. hydrocarbons.	—	—	More stable thermally than Zr analogs.	*107*
$(dmpe)_2HfH_3$ $C_6H_6/H_2/400$	Hf(benzyl)$_4$/dmpe/ atm/90°C	Tan solid.	—	1300 (Hf–H–Hf?)		*49*

monohydride chloride $Cp_2Hf(H)Cl$ has been prepared by the action of $LiAlH_4$ on Cp_2HfCl_2 and, as expected, it shows similar reactions to the zirconium analog in reactions with alkenes and alkynes. For example, with 1-heptene it yields $Cp_2HfCl[(CH_2)_6Me]$, which on treatment with bromine liberates the alkyl bromide $Me(CH_2)_6Br$ (*119*).

Reference has already been made to $Cp_2Zr(H)BH_4$; preliminary results have shown that a similar hafnium compound may be obtained (*73*). The hafnium dihydride is polymeric like $(Cp_2ZrH_2)_x$, and may also be prepared by hydrogenolysis of Cp_2HfMe_2 (*107*). The dihydrides $(C_5H_4R)_2HfH_2$ [R = Me, Me_2CH, Me_3C, $C_6H_5CH_2$, $C_6H_5(Me)CH$ (two stereoisomers)] have been obtained by the same reaction used for the zirconium compounds, namely treatment of the corresponding dichloride with methyllithium followed by treatment with hydrogen under pressure (*107*). The trihydride $(dmpe)_2HfH_3$ has been included in the general patent referred to earlier (*49*).

II. Vanadium, Niobium, and Tantalum Hydrides

The chemistry of hydrido complexes of group V metals seems to reflect the usual tendency for vanadium to behave differently from the other two elements, although generalizations are probably premature in such a new field. Certainly niobium and tantalum form numerous hydrides of similar composition and properties, appearing to have no vanadium counterparts to date, but there have been no systematic investigations involving all three elements under comparable conditions, as is clear from the following discussions.

A. VANADIUM HYDRIDE COMPOUNDS

Compounds containing vanadium–hydrogen bonds were first reported in the early 1960s, but only recently have any been reasonably well characterized. With one exception, all such compounds involve carbon monoxide (or the equivalent π-acceptor, PF_3) as coligands, and many also contain chelating phosphines or arsines, or the cyclopentadienyl moiety. Those compounds containing terminal vanadium–hydrogen bonds show characteristic ^{1}H-NMR absorption in the region τ 13.5–18.5, except for the trihydrides ($\tau = 8.86$), but no infrared absorptions attributable to $\tilde{\nu}_{M-H}$ have been reported. The spectroscopic properties of each of the vanadium hydrides are summarized in Table IV, together with other relevant information.

In the treatment that follows, the monohydrides are considered first,

TABLE IV

VANADIUM HYDRIDE COMPLEXES

Compound	Preparation	Properties	^{1}H NMR (τ, M–H)	Infrared (cm^{-1})	Comments	References
$HV(CO)_6$	$V(CO)_6$ + (1)Na/Hg + (2)H_3PO_4				Acidity functions measured but only salts are well characterized.	*120, 121*
$HV(CO)_5(PPh_3)$	$V(CO)_6/PPh_3$ + (1)Na/Hg + (2)H_3PO_4					
$HV(PP_3)_6$	$V(CO)_6^-$ + PF_3 + irradiation + protonation	Pale-yellow crystals, sublimes 60°C (10^{-2} torr), stable to 135°C.	18.4 multiplet [solution in $Ni(PF_3)_4$]	$\tilde{\nu}_{P-F}$ 846, 911	Diamagnetic, X_M -236×10^{-6} cm^3 mol^{-1}; mass spec. shows $HV(PF_3)_6^+$ but not $V(PF_3)_6^+$.	*122*
$HV(CO)_4$(dppm)	$[Et_4N][V(CO)_4$(dppm)] protonation	Yellow crystals, m.p. 75–82°C (dec), stable under N_2 at 10°C, turns brown in days at room temperature.	15.04 triplet (THF-d_8, 20°C); 14.37 triplet (benzene-d_6); $^2J(^1H-^{31}P)$ 21.9 Hz.	$\tilde{\nu}_{C-O}$ 1989, 1901, 1875, 1857 (0.02 *M* THF) or 1990, 1885, 1858, 1815 (KBr)	^{51}V NMR reported	*123, 124*
$HV(CO)_4$(dppe)	$[Et_4N][V(CO)_4$(dppe)] protonation	Yellow solid changing (r.t.) to brown (with no detectable spectral changes, *123*) or green/black [$V(CO)_4$dppe] (*125*); solutions deteriorate rapidly.	15.03 triplet (THF-d_8, 20°C); $^2J(^1H-^{31}P)$ 26.0 Hz.	$\tilde{\nu}_{C-O}$ 1990, 1878 (0.02 *M* THF) or 1988, 1890, 1867, 1856 (Nujol)	^{51}V NMR reported	*123, 125*
$HV(CO)_4$(dppp)	$[Et_4N][V(CO)_4$(dppp)] protonation	Yellow solid (turning brown at r.t.).	14.91 triplet (THF-d_8, 20°C); $^2J(^1H-^{31}P)$ 25.9 Hz.	$\tilde{\nu}_{C-O}$ 1990, 1909, 1867, 1831 (0.02 *M* THF)	^{51}V NMR	*123*
$HV(CO)_4$(dppb)	$[Et_4N][V(CO)_4$(dppb)] protonation	Yellow solid (turning brown at r.t.).	15.15 triplet (THF-d_8, 20°C); $^2J(^1H-^{31}P)$ 26.7 Hz.	$\tilde{\nu}_{C-O}$ 1988, 1895, 1867, 1839 (THF)	^{51}V NMR	*123*

$HV(CO)_4(dmpe)$	$[Et_4N][V(CO)_4(dmpe)]$ *protonation*	Pale-yellow crystals stable under N_2 (r.t.) (turns brown in air); toluene solutions stable under Ar (0°C); m.p. 123°C (dec).	14.58 triplet (toluene, d_8, 20°C); $^2J(^1H-^{31}P)$ 23.4 Hz.	$\tilde{\nu}_{C-O}$ 1981, 1865 (THF) or 1973, 1863, 1842 (Nujol)	NMR shows no temperature dependence between +20 and −65°C.	*126*
$HV(CO)_4(arphos)$	$[Et_4N][V(CO)_4(arphos)]$ protonation	Yellow crystals similar to (dppm) complex.	15.08 doublet (THF-d_8, 20°C); 14.53 doublet (benzene-d_6); $^2J(^1H-^{31}P)$ 25.9 Hz.	$\tilde{\nu}_{C-O}$ 1990, 1875 (THF) or 1985, 1885, 1868, 1852, 1822 (KBr)	^{51}V NMR	*123, 127*
$HV(CO)_4(diars)$	$[Et_4N][V(CO)_4(diars)]$ protonation	Pale-yellow crystals stable under N_2 (r.t.). Solutions air sensitive, but toluene solutions under Ar are stable (0°C).	14.48 singlet (toluene, d_8, 20°C).	$\tilde{\nu}_{C-O}$ 1989, 1975 (THF) or 1989, 1900, 1863, 1830 (Nujol)	NMR shows no temperature dependence between +20 and −67°C.	*123, 126*
$HV(CO)_3PhP(CH_2CH_2PPh_2)_2$	As for diphosphines	Yellow crystals	14.54 sextet (THF-d_8, 60°C); $^2J(^1H-^{31}P)$ 20 and 39.7 Hz.	$\tilde{\nu}_{C-O}$ 1927, 1920, 1835, 1820 (THF)	^{51}V NMR δ −1640 ^{31}P NMR δ +90	*123, 124*
$HV(CO)_3MeC(CH_2PPh_2)_3$	As for diphosphines	Yellow	15.06 (broad)	$\tilde{\nu}_{C-O}$ 1908, 1825, 1810	^{51}V NMR δ −1528 ^{31}P NMR δ +27, −28	*124*
$HV(CO)_4MeC(CH_2PPh_2)_3$	As for diphosphines		15.20 (triplet); $^2J(^1H-^{31}P)$ 26.1 Hz.	$\tilde{\nu}_{C-O}$ 1987, 1866	^{51}V NMR δ −1608	*124*
$HV(CO)_4P(CH_2CH_2PPh_2)_3$	As for diphosphines		15.32 (triplet); $^2J(^1H-^{31}P)$ 25 Hz.	$\tilde{\nu}_{C-O}$ 1991, 1877	^{31}P NMR δ +87, +76, −15.6	*124*
$HV(CO)_3P(CH_2CH_2PPh_2)_3$	As for diphosphines	Red needles	14.54 (sextet); $^2J(^1H-^{31}P)$ 39.7, 20.0 Hz.	$\tilde{\nu}_{C-O}$ 1922, 1911, 1819	^{51}V NMR δ −1690 ^{31}P NMR δ +99, +83, −15.6	*124*
$HV(CO)_4(Ph_2PCH_2CH_2PPhCH_2)_2$	As for diphosphines	Yellow powder	15.20 (triplet); $^2J(^1H-^{31}P)$ 23.0, 27.0 Hz.	$\tilde{\nu}_{C-O}$ 1990, 1905, 1877, 1845	^{51}V NMR δ −1685 ^{31}P NMR δ +68	*124*
$HV(CO)_3(Ph_2PCH_2CH_2PPhCH_2)_2$	As for diphosphines		15.08 (quartet); $^2J(^1H-^{31}P)$ 29.2, 21.4, 32.1 Hz.	$\tilde{\nu}_{C-O}$ 1905, 1806	^{51}V NMR δ −1665 ^{31}P NMR δ +96, +84, +80, −15.1, −18.0	*124*

(table continues)

TABLE IV (Continued)

Compound	Preparation	Properties	^{1}H NMR (τ, M–H)	Infrared (cm^{-1})	Comments	References
cis-$HV(CO)_2P(CH_2CH_2PPh_2)_3$	Irradiation of $HV(CO)_3$-$P(CH_2CH_2PPh_2)_3$	Red crystalline powder	13.84 (quartet of doublets); $^2J(^1H-^{31}P)$ 39.7, 9.6 Hz.	$\tilde{\nu}_{C-O}$ 1829, 1772	^{51}V NMR δ −1541 ^{31}P NMR δ +100	*124*
trans-$HV(CO)_2(Ph_2PCH_2CH_2PPhCH_2)_2$	Irradiation of $HV(CO)_3$-$(Ph_2PCH_2CH_2PPhCH_2)_2$	Red needles	13.62 triplet of triplets; $^2J(^1H-^{31}P)$ 113.0, 17.7.	$\tilde{\nu}_{C-O}$ 1884, 1764	^{51}V NMR δ −1658 ^{31}P NMR δ +111, +98	*124*
$HV(CO)_3$(mesitylene)	$[V(CO)_4$(mesitylene)]-PF_6 + (1) NaI and (2) $NaBH_4$ or Na/Hg	Orange solid stable in air (−20°C) but decomposing slowly at +25°C. Dec. under vac 69°C. THF solutions stable (under Ar). Other solutions dec. at 25°C. Toluene stable at −20°C.	15.8	$\tilde{\nu}_{C-O}$ 1961, 1895, 1879 (hexane)	NMR line-width is temperature-dependent. Mass spec. shows strong peaks for $[HV(CO)_n$-$(mesit)^+]$ and $[V(CO)_n(mesit)^+]$ where n = 0, 1, 2, 3.	*128*
$[CpV(H)(CO)_3]^-$	(a) $CpV(CO)_4$ + (1) Na/Hg + (2) H_2O + (3) pptn. as PPN^+ salt; or (b) $CpV(CO)_4$ electrolysis in THF/H_2O; or	PPN^+ salt is orange-yellow, m.p. (dec) 201°C. Air sensitive as solids or in solution (THF).	16.10 (THF, d_8)	$\tilde{\nu}_{C-O}$ 1890, 1780 (THF)	NMR line-width is temperature dependent.	*129–131*
	(c) $Na_2[CpV(CO)_3]$ + Et_4NCl in CH_3CN at room temperature	Et_4N^+ salt is relatively air stable. Slow decomposition (2 days) in solution (THF or CH_3CN).	16.33(Et_4N^+ salt)	$\tilde{\nu}_{C-O}$ 1889, 1775		*124*

$\{[CpV(CO)_3]_2H\}^-$	$CpV(CO)_4$ + $[CpV(H)(CO)_3]^-$ + uv irradiation or $[CpV(H)(CO)_3]^-$ plus bromoalkanes	Very reactive materials spectroscopically observed but not isolated.		$\tilde{\nu}_{C-O}$ 1857, 1817		*129, 130*
$Cp_2V(H)(\mu\text{-}Cl)_2AlCl_2$	Cp_2VCl_2 + Et_2AlCl_2 in CH_2Cl_2/*n*-heptane	Reactive intermediate observed by ESR.			ESR study	*132, 133*
$CpV(H)_2(CO)_3$	$[CpV(H)(CO)_3]^-$ + H^+	Suggested as an intermediate.				*130, 134*
$[H_2V(CO)_4(diars)]^+$	$[HV(CO)_4(diars)]$ + H^+	Postulated intermediate.				*135*
$H_3V(CO)_3(diars)$	$[Et_4N][V(CO)_4(diars)]$ plus excess HX(X = Cl, Br, or I) in THF	Red-violet crystals stable in air (r.t.) for several weeks. Under Ar, stable to 130°C.	8.86 triplet (CH_2Cl_2, D_2, −20°C).	$\tilde{\nu}_{C-O}$ 1840, 1779 (THF)	NMR linewidth very temperature dependent.	*126, 135*
$H_3V(CO)_3(dmpe)$	$[HV(CO)_4(dmpe)]$ plus *t*-butyl chloride/H_2O	Unstable violet-red solid.		$\tilde{\nu}_{C-O}$ 1827, 1740 (THF)	Spectra similar to $H_3V(CO)_3(diars)$.	*135*
$Cp_2V(\mu\text{-}H)_2BH_2$	$Cp_2VCl_2/NaBH_4$	Dark-violet pyrophoric solid		$\tilde{\nu}_{B-H_t}$ 2442, 2418 $\tilde{\nu}_{B-H_b}$ 1745, 1650	Mol. weight (cryoscopy), Raman spectrum. ^1H NMR shows all BH_4 protons equivalent (r.t.) at $\tau = 19.46$.	*136, 137*
	(a) $[PPN^+][CpV(H)(CO)_3]^-$ $BH_3 \cdot THF$ (b) $CpV(CO)_4$ + $PPN^+BH_4^-$ (irradiation)	Green crystals (PPN^+ salt)	5.86 (Cp) 2.48 (PPN^+)	$\tilde{\nu}_{C-O}$ 1846, 1735 (THF) $\tilde{\nu}_{C-O}$ 1835, 1721 (KBr) $\tilde{\nu}_{B-H}$ 2360 (KBr)	Elemental analysis.	*130*
$[V(BH_4)_3]$?						*138, 139*

followed by the di- and trihydrides, and the section concludes with discussion of compounds containing bridging $V-(H)_n-BH_m$ linkages.

1. Monohydrides of Vanadium

a. $HV(CO)_6$ *and* $HV(CO)_5(PPh_3)$. Protonation of carbonyl anions is a well-established general route to hydride complexes and has been used for the production of these vanadium compounds: $V(CO)_6^-$ can be made from $V(CO)_6$ by reduction with sodium amalgam, or from VCl_3 by reaction with sodium and carbon monoxide in diglyme at 160°C; $V(CO)_5(PPh_3)^-$ can be prepared by treatment of $V(CO)_6$ with triphenylphosphine (1:3 mole ratio) in hexane, followed by reduction with sodium amalgam. Phosphoric acid has been found to be the most convenient protonating agent for either anion.

Although numerous metal salts of these acids have been made and analyzed, the acids themselves are poorly characterized. However, it is known that they are strongly acidic, as indicated by their pK_a values, which have been determined potentiometrically (*120, 121*).

b. $HV(PF_3)_6$. In view of the similar ligand properties of CO and PF_3, it is not surprising to find that this complex has been produced in an analogous manner to that used for the carbonyl hydride:

$$[Na(diglyme)_2]^+[V(CO)_6]^- \xrightarrow[\text{UV, diglyme}]{PF_3} [V(PF_3)_6]^- \xrightarrow{H_3PO_4} HV(PF_3)_6$$

The ^{1}H-NMR spectrum [in $Ni(PF_3)_4$] showed a characteristic hydride resonance at $\tau = 18.4$, and the mass spectrum showed the molecular ion and fragments derived by successive loss of PF_3 from the ions $[HV(PF_3)_5]^+$ and $[V(PF_3)_5]^+$ but gave no indication of $[V(PF_3)_6]^+$. The compound is thermally stable to at least 135°C (*122*).

c. $[HV(CO)_m$(phosphine)] *complexes and related compounds involving arsenic ligands.* Compounds of this nature are known for a variety of "di-," "tri-," and "tetraphosphines" and some arsenic analogs. For the diphosphines and diarsines, only tetracarbonyls (**XXIV – XXX**) have been reported; but when "tri-" or "tetraphosphines" are employed, $m = 2, 3$, or 4 carbonyls (**XXXI – XXXIX**) are known, though in these cases the tetracarbonyls appear to be the least stable.

d. "Diphosphine" compounds: $[HV(CO)_4\widetilde{PP}]$($\widetilde{PP} = Ph_2P(CH_2)_nPPh_2$; $n = 1-4$; **XXIV–XXVII**); $HV(CO)_4\{Me_2P(CH_2)_2PMe_2\}$ (**XXVIII**); $HV(CO)_4\{Ph_2As(CH_2)_2PPh_2\}$, (**XXIX**); *and* $HV(CO)_4$(diars), (**XXX**). Various methods of preparation have been reported for these compounds, but all involve protonation of the corresponding "phosphine" carbonylate anions, and they differ only in the manner in which this has been accomplished. Treatment of the anions with silica gel, presumably by virtue of potentially acidic {Si—OH} groups, has proved a convenient method for compounds (**XXIV**)-(**XXIX**) (*123, 124*). Other means have included *t*-butyl chloride and water (for **XXV** and **XXVII**) (*125, 126*), and $Ph_2AsHCl_2 \cdot 2H_2O$ in benzene (for **XXX**) (*123, 126*).

The hydrides are described as microcrystalline yellow powders, which change to ochre or brown upon standing at room temperature. These color changes are not accompanied by any observable changes in the infrared or NMR spectra (*123*) unless the storage is prolonged, in which case more profound changes may occur. For example, (**XXV**) is converted to paramagnetic green-black $V(CO)_4$(dppe) (*125*). At lower temperatures (−10°C), and under N_2, the solid complexes are stable for at least several months; however, solutions of the hydrides deteriorate rapidly unless oxygen is rigorously excluded. Room-temperature ^{1}H-NMR (THF-d_8) spectra reveal the hydridic resonance in the range $\tau = 14.5$ to $\tau = 15.15$ and have been interpreted for compounds (**XXIV**)-(**XXVIII**) as showing either a fluxional motion of the hydride about the entire seven-vertex polyhedron or that the hydride is fixed so that the two phosphorous atoms are magnetically equivalent with respect to it (*123*). However, the ^{1}H-NMR spectrum of (**XXX**) shows no evidence of fluxionality, since there is no change in the $\tau = 14.48$ resonance between +20°C and −67°C (*126*). ^{31}P-NMR and ^{51}V-NMR spectra were also obtained for all compounds but add little to the conclusions reached from the proton spectra (*123, 124*).

The hydrides readily lose their hydrogen upon reaction with other materials. In some cases, the hydrogen is transferred to the reactant, which then occupies the coordination position originally held by the hydride ligand (*127*), e.g., $HV(CO)_4\widetilde{PP} + Et_3N \rightarrow HNEt_3V(CO)_4PP$ and $HV(CO)_4$(dppm) + isoprene → (η^3-dimethylallyl)$V(CO)_3$(dppm).

e. "Triphosphine" compounds: $HV(CO)_3PhP(CH_2CH_2PPh_2)_2$, (**XXXI**); $HV(CO)_3MeC(CH_2PPh_2)_3$, (**XXXII**). These compounds have been made by the silica-gel protonation method used for their diphosphine counterparts (*123, 124*), and their ^{1}H-, ^{31}P- and ^{51}V-NMR spectra have been interpreted in favor of a model involving restricted dynamic behavior based on a hydride-face-capped octahedron similar to that of $HTa(dmpe)_2(CO)_2$ (*124*).

f. "Tetraphosphine" compounds: $HV(CO)_4P(CH_2CH_2PPh_2)_3$, (**XXXIV**); $HV(CO)_3P(CH_2CH_2PPh_2)_3$, (**XXXV**); $HV(CO)_4(Ph_2PCH_2CH_2PPhCH_2)_2$, (**XXXVI**); $HV(CO)_3(Ph_2PCH_2CH_2PPhCH_2)_2$, (**XXXVII**); *cis*-$HV(CO)_2P(CH_2CH_2PPh_2)_3$, (**XXXVIII**); *and trans*-$HV(CO)_2(Ph_2PCH_2)$-

$CH_2(PPhCH_2)_2$, (**XXXIX**). Compounds (**XXXIV**)–(**XXXVII**) have been made via the silica-gel protonation route just described, and the dicarbonyl complexes (**XXXVIII**) and (**XXXIX**) by UV irradiation of their tricarbonyl analogs (*124*).

g. $HV(CO)_3$*(mesitylene).* This compound is obtained as a bright orange powder (decomp. 69–72°C) from the reaction of $[IV(CO)_3$(mesitylene)] with $NaBH_4$ in THF at 0°C. It shows a characteristic hydride resonance at $\tau = 15.8$ (toluene), and further evidence of its nature is found in its conversion to $[V(CO)_3(\text{mesitylene})]^-$, isolable as the tetrabutylammonium salt, by either sodium amalgam or sodium hydroxide (*128*).

h. $[CpV(H)(CO)_3]^-$ *and* $[\{CpV(CO)_3\}_2H]^-$. Treatment of a slurry of $Na_2[CpV(CO)_3]$ in THF with 1 eq H_2O yields solutions containing $[CpV(H)(CO)_3]^-$, which may be isolated as its orange-red $(Ph_3P)_2N^+$ salt. A corresponding deuteride is produced if D_2O is used (*129, 130*). More recently it has been found that a higher yield, in a more air-stable form (as the Et_4N^+ salt), results from the reaction of $Na_2[CpV(CO)_3]$ with Et_4NCl in acetonitrile (*124*). The ion also is produced during the electrolysis in THF/H_2O of either $CpV(CO)_4$, or $Cp_2V(CO)$ under a CO atmosphere (*131*). Irradiation of this species in the presence of $CpV(CO)_4$ produces $[\{CpV(CO)_3\}_2H]^-$, which is believed to be a V–H–V bridged dimer, although it has not been fully characterized. Due to its extreme sensitivity, it has not been isolated from solution (*130*).

The ^1H-NMR spectrum of $[CpV(H)(CO)_3]^-$ shows the hydride resonance at $\tau = 16.10$, and the nature of the ion has been further demonstrated by its chemical reactions. For example,

$$[CpV(H)(CO)_3]^- + RX \rightarrow RH + \text{organometallics}$$

and

$$[CpV(H)(CO)_3]^- + RCOX \rightarrow RCHO + \text{organometallics}$$

where R is an alkyl group. The hydrogen acquired by the R or RCO group is established as coming from the hydride (not the solvent) by reactions of the deuteride analog, e.g., $[CpV(D)(CO)_3]^-$ + 1-bromooctane → $C_8H_{17}D$. The organometallic products of these reactions are complex and include the bridged dimer and $CpV(CO)_4$. A detailed kinetic and mechanistic study of these reactions has been carried out (*130*).

i. $Cp_2V(H)(\mu\text{-}Cl_2)(AlCl_2)$. The reaction between Cp_2VCl_2 (in methylene chloride) and Et_2AlCl_2 (in heptane) yields a paramagnetic product designated as the hydrido complex on the basis of its ESR spectrum (77 K). The molecule has a distorted trigonal bipyramidal structure with C_{2v} symmetry (*132*). The ESR spectrum had been reported previously but was not assigned at that time (*133*).

j. $\{\mathrm{CpV(H)_2(CO)_3}\}$. This transient species was mentioned in 1970 by Fischer (*134*), and again by Bergman and co-workers in 1978 (*130*). There is as yet no direct evidence for its existence, but it may be produced in this reaction (*130*):

$$[\mathrm{CpV(H)(CO)_3}]^- \xrightarrow{\mathrm{H}^+} [\mathrm{CpV(H)_2(CO)_3}] \xrightarrow{-\mathrm{H}_2} \mathrm{CpV(CO)_3}.$$

k. $[\mathrm{H_2V(CO)_4(diars)}]^+$. This and related species have been considered as possible intermediates in the reactions in which $\mathrm{HV(CO)_4(diars)}$ is converted by HX into the trihydride, by the scheme outlined here (*135*):

$$\mathrm{HV(CO)_4(diars)} \xrightleftharpoons{+\mathrm{HX}} \mathrm{H_2V(CO)_4(diars^+)X^-} \rightleftharpoons \mathrm{HV(CO)_3(diars)[C(OH)X]} \xrightleftharpoons{+\mathrm{HX}}$$
$$\mathrm{H_2V(CO)_3(diars)[C(OH)X_2]} \rightleftharpoons \mathrm{H_3V(CO)_3(diars)} + \mathrm{COX_2}$$

l. $\mathrm{H_3V(CO)_3(diars)}$. This compound is produced in good yield from protonation reactions of $\mathrm{(Et_4N)[V(CO)_4(diars)]}$ with either anhydrous or aqueous HX (X = Cl, Br, or I) in THF solution (*135*). A mechanism for this reaction is suggested above. The trihydride gives a strongly temperature-dependent ^{1}H-NMR signal at $\tau = 8.86$ attributable to the hydrides.

In contrast to the other carbonyl hydrides of vanadium, $\mathrm{H_3V(CO)_3}$-(diars) is remarkably thermally stable and resistant to deprotonation. Even *n*-butyllithium fails in this regard, though it is possible to replace two of the hydrogens in the photochemical reaction

$$\mathrm{H_3V(CO)_3(diars)} + \mathrm{CO} \xrightarrow{\mathrm{UV}} \mathrm{HV(CO)_4(diars)} + \mathrm{H_2}$$

The latter reaction is reminiscent of the way in which $\mathrm{Cp_2M(H)(L)}$ complexes of niobium and tantalum are formed from $\mathrm{Cp_2MH_3}$. However, this seems to be the only similarity between the vanadium trihydride and $\mathrm{Cp_2MH_3}$ (M = Nb,Ta).

m. $\mathrm{H_3V(CO)_3(dmpe)}$. This violet-red compound, produced by protonation of $\mathrm{HV(CO)_4(dmpe)}$ by *t*-butyl chloride and water,† has an infrared spectrum very similar to that of the (diars) compound, and it is on this basis that its composition was deduced (*135*).

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† Interestingly, protonation by aqueous HX is not successful; instead decomposition to vanadium salts is observed.

n. $Cp_2V(\mu\text{-}H)_2BH_2$ *and* $[CpV(CO)_2(\mu\text{-}H)_2BH_2]^-$. These well-characterized compounds have recently been reported (*130, 136, 137*). The former is produced when $LiBH_4$ reacts with Cp_2VCl_2 at −12°C in 1,2-dimethoxyethane, and an analogous (BD_4) complex is also known. The violet crystalline materials decompose slowly at room temperature even under nitrogen, but infrared, Raman, and NMR studies have been performed and have revealed bidentate coordination of the BH_4 group. Although all four protons are equivalent at room temperature (τ = 19.46), the barrier to bridge-terminal hydrogen exchange is high enough to permit observation of the instantaneous structure in the low-temperature (−100°C) ^{1}H-NMR spectrum. At this temperature, the bridge hydrogens show $\tau \approx 34$ and the terminal ones are calculated to lie at $\tau \approx 5$ (obscured by the solvent). The infrared and Raman spectra indicate that the bridge expansion (involving the VH_2B segment, and having considerable $\bar{\nu}_{M-H}$ character) occurs at 1395 cm^{-1} (1030 cm^{-1} for the deuterated material) (*136, 137*). The second compound results when mixtures of $CpV(CO)_4$ and $[(Ph_3P)_2N^+BH_4^-]$ are irradiated. However, a better method starts with $[CpV(H)(CO)_3]^-$, which is reacted with THF · BF_3. The $(Ph_3P)_2N^+$ salt is green and shows spectra similar to $Cp_2V(\mu\text{-}H)_2BH_2$; its composition is based upon these similarities, its elemental analysis, and its method of preparation. Reactions leading to each compound are thought to proceed via $[Cp(CO)_3V\text{—}H\text{—}BH_3]^-$ (*130*).

o. $V(BH_4)_n$. Finally, mention should be made of the compound $V(BH_4)_n$, which was originally (*138*) considered to be a V(III) material but is now reported as $V(THF)_x(BH_4)_2$, containing V(II) (*139*).

B. NIOBIUM HYDRIDE COMPOUNDS

Niobium forms more than 30 compounds in which either terminal niobium–hydrogen or bridging Nb–$(\mu\text{-}H)_n$–M linkages (M is another metal or boron; n = 1, 2, or 3) are present. Although most contain only one Nb–hydrogen bond, up to five per molecule are known; but even in the latter, some other ligands are always present and the nature of the co-ligands is clearly important in determining the stability of all the hydrido niobium complexes. Cyclopentadienyl groups are present in nearly all cases [the exceptions involve the chelating phosphine $Me_2PCH_2CH_2PMe_2$, (dmpe)], together with additional two-electron donors such as carbon monoxide, alkenes or alkynes, and monophosphines. However, the exact role of these co-ligands is not clear, and the discovery of most compounds owes more to serendipity than to rational synthesis.

The terminal hydrides display a $\bar{\nu}_{Nb-H}$ infrared absorption in the range 1620–1740 cm^{-1} [falling to 1520–1550 for the (dmpe) compounds], and ^{1}H-NMR absorption attributable to the hydride ligands in the τ range 10.8–17.8. The latter rises to 17–22 for the bridged compounds. Specific data for the compounds are found in Table V. The pattern used in the discussion of the vanadium hydrides is continued, so that the treatment begins with monohydrides and ends with the bridged species.

1. Simple Hydrides

a. $HNb(dmpe)_2(CO)_2$ *and* $HNb(dmpe)_2(C_2H_4)_2$. These compounds are produced from $Me_5Nb(dmpe)$ according to the equations

$$Me_5Nb(dmpe) + H_2 + dmpe \xrightarrow[60°C]{THF} H_5Nb(dmpe)_2$$

$$H_5Nb(dmpe)_2 + 2L \xrightarrow[25°C]{pentane} HNb(dmpe)_2(L)_2 + 2H_2$$

where L = CO or C_2H_4; the $(C_2D_4)_2$ complex can also be made.

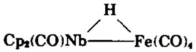
The infrared spectra of the compounds show a weak to medium band at 1550 cm^{-1} attributable to the Nb–H stretch. The carbonyl band is strong and occurs at 1700–1750 cm^{-1}; the olefinic ν_{C-H} stretching mode shows up as a shoulder at 3020 cm^{-1}, absent in the (C_2D_4) spectrum, which shows peaks at 2290, 2220, 2200, and 2170 cm^{-1} due to coordinated olefin. The ^{1}H-NMR spectrum of $HNb(dmpe)_2(CO)_2$ in C_6D_6 at 25°C shows a triplet of triplets at $\tau = 14.46$ for the hydride resonance. This shifts to $\tau = 12.94$ in the olefin complexes. These findings are analogous to those for the corresponding $HTa(dmpe)_2L_2$, complexes which are isomorphous (and, presumably, isostructural) with the niobium compounds. ^{31}P-NMR and ^{13}C-NMR studies have also been performed on these materials. It is noteworthy that the exchange of hydrogen between the hydride and the olefin in $HNb(dmpe)_2(C_2H_4)_2$ is much slower than in the isoelectronic $[HMo(dppe)_2(C_2H_4)_2]^+$. The hydride τ12.94 resonance of the niobium compound shows no broadening characteristic of the onset of exchange with ethylene protons, in marked contrast to that seen in the molybdenum complex, where four protons on one of the ethylene ligands equilibrate with the hydride ligand [rapidly on the ^{1}H-NMR timescale (100 MHz) at +7°C] by the postulated reversible formation of an ethyl ligand (*140, 141*).

b. $[Cp_2Nb(H)L]$ *complexes.* Hydrido compounds of this general formula are known where L = CO (*142–144*), an alkene (various) (*145, 146*), an alkyne (various) (*147*), or a phosphine (various) (*142, 145, 148*). A η^2-COT complex has been postulated as an intermediate in the

TABLE V

NIOBIUM HYDRIDE COMPLEXES

Compound	Preparation	Properties	^{1}H NMR (τ, M–H)	Infrared (cm^{-1})	Comments	References
$HNb(CO)_2(dmpe)_2$	$H_3Nb(dmpe)_2/CO$	Orange needles.	14.46 triplet of triplets (benzene-d_6, 25°C); ^2J ($^1H-^{31}P$) 14, 92 Hz.	$\tilde{\nu}_{Nb-H}$ 1550 (Nujol) $\tilde{\nu}_{C-O}$ 1700–1750	^{31}P NMR, partial X-ray.	*140, 141*
$HNb(C_2H_4)_2(dmpe)_2$	$H_5Nb(dmpe)_2/C_2H_4$	Yellow crystals.	12.94 triplet of triplets (benzene-d_6, 25°C); ^2J ($^1H-^{31}P$) 21, 102 Hz.	$\tilde{\nu}_{Nb-H}$ 1550 (Nujol) $\tilde{\nu}_{C-H}$ 3020	C_2D_4 complex also made. ^{31}P and ^{13}C NMR.	*140, 141*
$Cp_2Nb(H)(CO)$	(a) Cp_2NbH_3/CO (in benzene) (b) Cp_2NbCl_2 + (1)BH_4^- and (2) NEt_3 + CO (in THF)	Violet-brown crystals (color depends on source of Cp_2NbH_3).	16.39 or 16.5	$\tilde{\nu}_{Nb-H}$ 1695	X-ray. ^{13}C NMR.	*142–144*
$Cp_2Nb(H)$ (alkene)	(a) Cp_2NbH_3/C_2H_4 (in benzene) (b) Cp_2NbCl_2/alkyl MgCl	Yellow crystals.	12.95 unresolved singlet (benzene-d_6)	$\tilde{\nu}_{Nb-H}$ 1735	X-ray of Et analog. ^{13}C NMR.	*145, 146, 153*
$Cp_2Nb(H)(RC{\equiv}CR')$	Cp_2NbH_3/acetylenes (in benzene)	Yellow crystals.	10.8	$\tilde{\nu}_{Nb-H}$ 1720 $\tilde{\nu}_{C-C}$ 1815	Various alkynes used.	*147*
$Cp_2Nb(H)(PEt_3)$	Cp_2NbH_3/Et_3P		17.69; $^2J(^1H-^{31}P)$ 29 Hz.	$\tilde{\nu}_{Nb-H}$ 1650		*145*
$Cp_2Nb(H)(PMe_3)$	Cp_2NbH_3/Me_3P		17.84; $^2J(^1H-^{31}P)$ 27 Hz.	$\tilde{\nu}_{Nb-H}$ 1635		*145*
$Cp_2Nb(H)(PPh_3)$	Cp_2NbCl_2 + (1) BH_4^- and (2) Ph_3P	Dark-red crystals.	16.65; $^2J(^1H-^{31}P)$ 27 Hz.	$\tilde{\nu}_{Nb-H}$ 1625		*148*
$Cp_2Nb(H)(PPhMe_2)$	Cp_2NbCl_2 + (1) BH_4^- and (2) $PhMe_2P$	Dark-red crystals.	17.53; $^2J(^1H-^{31}P)$ 28.6 Hz.	$\tilde{\nu}_{Nb-H}$ 1630		*148*
$Cp_2Nb(H)(PPh_2Me)$	Cp_2NbH_3/PPh_2Me (in benzene)		17.7 doublet; $^2J(^1H-^{31}P)$ 29 Hz (benzene-d_6).			*142*
$Cp_2Nb(H)(\eta^2COT)$	$Cp_2Nb(C_8H_9)/NaBH_4$	Postulated intermediate.				*149*
Cp_2NbH	$Cp_2Nb(BH_4)/Et_3N$	Postulated 16-electron intermediate.				*170*; see also *162*
$[HNb(\eta^5\text{-}Cp)(\eta^{1,5}\text{-}C_5H_4)]_2$	Cp_2NbH_3 heat to 80° (benzene); Cp_2NbCl_2/Na naphthalene/THF/−50°C.	Yellow crystals.	12.07 (benzene-d_6).	$\tilde{\nu}_{Nb-H}$ 1680 (*145*) or 1650 (*154*)	"Niobocene"; X-ray; diamagnetic.	*145, 154–156*
$Cp_2Nb(H){=}C(H)OZr(H)Cp^{\ddagger}_2$ ($Cp^{\ddagger} = C_5Me_5$)	$Cp_2Nb(H)(CO)/Cp^{\ddagger}_2ZrH_2$/toluene/−80°C		13.14	$\tilde{\nu}_{Nb-H}$ 1701 $\tilde{\nu}_{Zr-H}$ 1567		*102*
$[CpNb(H)(dmpe)(CO)_2]^+$	Protonation of $CpNb(dmpe)(CO)_2$	PF_6^- salt is yellow; easily deprotonated.				*158*
$Cp_2Nb(H)(t\text{-butyl})$ $Cp_2Nb(H)(Cl)$ $Cp_2Nb(H)(allyl)$ Cp_2NbH_2	$Cp_2NbH_3 \xrightarrow{\Delta} Cp_2NbH_2$; Cp_2NbH_2 + L: e.g., $Cp_2NbH_2 + C_3H_6 \rightarrow Cp_2Nb(H)(C_3H_7)$	Transient paramagnetic species identified by ESR.			ESR study	*160, 161*
$CpNb(H)_2(CO)(PPh_3)_2$	Photochemical reaction of Cp with $CpNb(CO)_2(PPh_3)_2$.				X-Ray	*159*

$[Cp_2Nb(H)_2(PR_3)]^+$	$Cp_2Nb(H)(PR_3)$ + aqueous HCl, salts pptd. with BF_4^- or PF_6^-.		13.96 doublet; $^2J(^1H-^{31}P)$ 31.5 Hz.	$\tilde{\nu}_{Nb-H}$ 1740	(PR_3=PPh_3 or $PPhMe_2$)	*148*
$[Cp_2Nb(H)_2(CO)]^+$	$Cp_2Nb(H)(CO)$/HCl (THF, <0°C)	Yellow solid stable below −30°C, decomposing instantly at r.t.				*152*
Cp_2NbH_3	(a) $NbCl_5$/NaCp/$NaBH_4$/H_2; or (b) Cp_2NbCl_2 + reducer + H_2O	White/pale-yellow [if $NaAlH_2(OR)_2$ used, color may be brown].	12.73 and 13.72 (toluene-d_8) or 12.62 and 13.5 (benzene-d_6)	$\tilde{\nu}_{Nb-H}$ 1710	X-Ray and neutron diffraction structure.	*142, 143, 145, 147, 162*
$H_5Nb(dmpe)_2$	$Nb(Me)_5(dmpe)/H_2$(500 atm)/THF/60°C	Pale-yellow waxy solid stable under N_2 (25°C) for several days. Dec. on prolonged standing at r.t.	12.04 quintet $^2J(^1H-^{31}P)$ 39 Hz (benzene-d_6, 25°C); or toluene-d_8, 80°C)	$\tilde{\nu}_{Nb-H}$ 1520 (Nujol)	^{31}P NMR	*140*
 $Cp_2(CO)Nb\overset{H}{—}Fe(CO)_4$	$Cp_2NbH_3/Fe(CO)_5$	Dark-brown prisms.	16.4 (toluene-d_8; not seen in benzene)	$\tilde{\nu}_{Nb-H}$ 1720	X-Ray of solid ^1H- and ^{13}C NMR suggest different structure in solution.	*163, 164*
$Cp_2Nb(\mu-H)_2HfR_3$	Cp_2NbH_3/HfR_4	Unstable; $t_{\frac{1}{2}}$ a few hours.			R=$PhCH_2$	*151*
$[Cp_2Nb(\mu-H)_2]_2Zn$	Cp_2NbH_3/Et_2Zn	Stable under N_2 (r.t.) for 1 week.	19.05			*151*
$Cp_2Nb(CO)(\mu H)Zn(BH_4)_2$	$NbCl_5$/NaCp/Zn plus (1) CO/THF, (2) $NaBH_4$	Yellow prisms.		$\tilde{\nu}_{Nb-H}$ 1400 $\tilde{\nu}_{C-O}$ 1960	X-Ray, mass spectrum.	*165*
$Cp_2Nb(\mu-H)_2BH_2$	$Cp_2NbCl_2/NaBH_4$/THF	Dark-green air-sensitive crystals.		$\tilde{\nu}_{B-H_t}$ 2450 $\tilde{\nu}_{B-H_b}$ 1745, 1628	X-Ray structure; mass spectrum; ^1H NMR.	*146, 148, 166, 167*
$Cp_2Nb(BH_4)(Cl)$	$NbCl_5$/NaCp/$LiBH_4$	Speculative, based on elemental analysis only.		$\tilde{\nu}_{B-H}$ 2460, 1900		*168*
$Cp_2Nb(CO)(\mu-H)BF_3$	$Cp_2Nb(H)(CO)/BF_3$	Red-violet crystals.		$\tilde{\nu}_{C-O}$ 1930		*150*
$Cp_2Nb(CO)(\mu-H)AlEt_3$	$Cp_2Nb(H)(CO)/Et_3Al$	Pyrophoric.	21.51 (benzene-d_6, 220 MHz)		Mol. weight (cryoscopy)	*151*
$Cp_2Nb(C_2H_4)(\mu-H)AlEt_3$	$Cp_2Nb(H)(C_2H_4)/Et_3Al$	Pyrophoric.	19.63 (benzene-d_6, 220 MHz)		Mol. weight (cryoscopy)	*151*
$Cp_2Nb(PMe_3)(\mu-H)AlEt_3$	$Cp_2Nb(H)(PMe_3)/Et_3Al$	Pyrophoric.	23.12 (benzene-d_6, 220 MHz)		Mol. weight (cryoscopy)	*151*
$Cp(\eta^{1,5}-C_5H_4)Nb(\mu-H)AlEt_3]_2$	"niobocene" dimer/Et_3Al	Pyrophoric solid.	17.02 (benzene-d_6, 220 MHz)		Mol. weight (cryoscopy)	*151*
$Cp_2Nb(\mu-H)_2AlEt_2$	(a) Cp_2NbH_3/Et_3Al (b) $Cp_2NbCl_2/NaAlH_2Et_2$	Orange crystals stable under N_2 (r.t.) air reactive.	21.4 or 22.78 (benzene-d_6)			*142, 151*
$Cp_2Nb(\mu-H)_2AlH_2$	$Cp_2NbCl_2/LiAlH_4$(THF)	Orange crystals	19.8 (benzene-d_6) or 21.1 (THF)			*142, 143*
$Cp_2NbH_3AlHEt_3$	$Cp_2NbCl_2/NaAlH_2Et_2$		14.5 and 15.0			*143*
$Cp_2NbH_3AlEt_3$	Cp_2NbH_3/Et_3Al	Stable only below −40°C.	13.6 and 15.3			*151*
$CsNb_6I_{11}H$				$\tilde{\nu}_{Nb-H}$ 1120		*169*

reaction of $Cp_2Nb(C_8H_8)$ with $NaBH_4$ (*149*). There is some evidence that Cp_2NbH is also produced in this reaction (*170*).

Syntheses. Most (and, presumably, all) of these compounds can be made from Cp_2NbH_3 according to the reaction

$$Cp_2NbH_3 + L \xrightarrow[\text{benzene}]{\text{reflux}} Cp_2Nb(H)L + H_2$$

However, some care must be taken where L = C_2H_4 as the ethyl/ethylene complex is the main product if excess ethylene is available (*142, 145, 147*). The more readily available Cp_2NbCl_2 has been used as a starting material in a general reaction, which produces the alkene complexes from the corresponding alkyl Grignard. To date, *n*-propyl, *i*-propyl, and *n*-butyl Grignards have been successfully used (*146*). Cp_2NbCl_2 was also the starting point for the production of some of the phosphine complexes (*148*), such as

$$Cp_2NbCl_2 \xrightarrow{NaBH_4} Cp_2Nb(BH_4) \xrightarrow{PPh_3} Cp_2Nb(H)(PPh_3)$$

Spectroscopic Properties. The infrared spectra of these $Cp_2Nb(H)L$ complexes contain a $\bar{\nu}_{Nb-H}$ band in the region 1630 cm^{-1} (for the phosphines) to 1730 cm^{-1} (for the olefin) (*142, 145*). Their ^1H-NMR spectra show a band due to the hydride hydrogen in the vicinity of $\tau 17$ (in the phosphines), but considerably lower for the olefins (12.95) and alkynes (10.8). The crystal structure of $Cp_2Nb(H)(CO)$ has been determined but the niobium-bonded hydrogen was not located (*144*). X-ray data are available for $Cp_2Nb(Et)(C_2H_4)$, which, at least in solution, is known to be similar to $Cp_2Nb(H)(C_2H_4)$ from ^1H and ^{13}C NMR studies (*153*).

Bonding. The bonding in $Cp_2M(H)(CO)$ and $Cp_2M(H)(C_2H_4)$ complexes has been discussed from the molecular-orbital viewpoint. It is of interest that such compounds are predicted only for those metals with two or fewer d electrons in the M(III) state (*79*).

Reactions. $Cp_2Nb(H)(CO)$ reacts with Lewis acids to produce compounds, of varying stability, in which the acid coordinates to the hydride ligand. For example,

$$Cp_2Nb(H)(CO) + BF_3 \xrightarrow{\text{toluene}} Cp_2Nb(CO)(HBF_3) \qquad \text{(Ref. } \mathit{150}\text{)}$$

$$Cp_2Nb(H)(CO) + AlEt_3 \longrightarrow Cp_2Nb(CO)(HAlEt_3) \qquad \text{(Ref. } \mathit{151}\text{)}$$

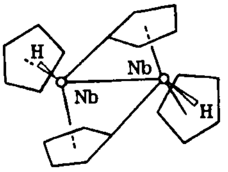
$$Cp_2Nb(H)(CO) + H^+ \xrightarrow[\text{THF, <0°C}]{\text{HCl}} \{Cp_2Nb(CO)(H_2)Cl\} \qquad \text{(Ref. } \mathit{152}\text{)}$$

The latter spontaneously decomposes to $Cp_2Nb(CO)Cl$ and H_2 at room temperature, and the aluminum compound is not much more stable.

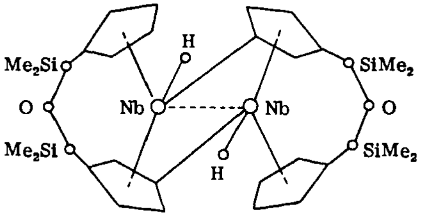
However, the boron adduct appears to be indefinitely stable under ambient conditions.

It was reported originally that $Cp_2Nb(H)(CO)$ reacted with H_2 to yield a brown material from which some methanol could be obtained (*142*); however, it is now known that the latter derived from an impurity present in the carbonyl hydride, which was made using $NaAlH_2(OCH_2CH_2OCH_3)_2$ and Cp_2NbCl_2. $Cp_2Nb(H)(CO)$ made by other methods shows no such impurity and generates no methanol-producing materials when reacted with H_2 (*143*). $Cp_2Nb(H)(C_2H_4)$ reacts with excess ethylene to yield the ethyl complex referred to above; however, in the presence of H_2, ethylene is catalytically reduced to ethane, probably via an unisolated $[Cp_2Nb(H)_2(Et)]$ intermediate (*145, 153*). $[Cp_2Nb(H)(alkyne)]$ complexes react nearly quantitatively with acid producing the corresponding cis olefins, possibly via an intermediate of the form $[Cp_2Nb(H)_2(alkyne)]^+$. When methyl salts are used, the product is methane rather than the methylated olefin, since the elimination of CH_4 from the intermediate $[Cp_2Nb(H)(Me)(alkyne)]^+$ occurs more rapidly than the insertion of alkyne into the Nb–H bond. The hydrido complexes are rapidly converted into their iodo analogs by CH_3I (*147*). In $[Cp_2Nb(H)(phosphine)]$ when the phosphine is Ph_3P or $PhMe_2$, and presumably in other cases too, protonation by dilute aqueous HCl in the presence of a suitable precipitating anion gives rise to salts such as $[Cp_2Nb(H)_2(PPhMe_2)]^+(PF_6^-)$, with $\tilde{\nu}_{Nb-H}$ at 1740 cm^{-1} and a doublet at $\tau = 13.96$ in the ^1H-NMR spectrum assignable to the NbH_2 hydrogens (*148*).

c. $[(HNb(\eta^5\text{-}C_5H_5)(\eta^{1,5}\text{-}C_5H_4)]_2]$. Thermal decomposition of Cp_2NbH_3 in benzene at 80°C, in the absence of other ligands, yields a yellow solid, to which the name "niobocene" has sometimes been applied since the compound's elemental analysis is consistent with the Cp_2Nb formulation. However, the observed diamagnetism and the ^1H-NMR spectrum rule out this idea. Instead, they suggest a dimer with bridging C_5H_4 groups and Nb–H linkages, and this has been confirmed by an X-ray diffraction study (*154, 155*). The presence of an M–H bond is also demonstrated by the infrared peak at 1650 cm^{-1} and the $\tau = 12.07$ ^1H-NMR resonance. The structure (idealized C_2 symmetry) is shown below. The Nb–H and Nb–Nb bond lengths are 1.70(3) and 3.105(6) Å,



respectively, and the structure can be viewed as derived from the typical Cp_2M moiety. It is interesting to compare with the similar titanium and zirconium compounds discussed above, particularly (**VIII**), where no Ti–H bonds are formed. Hydrogenation of niobocene at 80°C (800 atm) in benzene regenerates Cp_2NbH_3, presumably via Cp_2NbH, although the latter has not been isolated (*145, 154, 155*). Niobocene has also been made by the reaction of Cp_2NbCl_2 with Na(Naphth) in THF at −50°C (*156*). The structure of the closely related compound has been



reported (*157*). The Nb–Nb distance is significantly longer, 3.932 Å compared to 3.105 Å in niobocene (*154*).

d. $Cp_2Nb(H){=}C(H)OZr(H)(C_5Me_5)_2$. This has been referred to (Section I,B,f), and is produced when $Cp_2Nb(H)(CO)$ reacts at −80°C with $H_2Zr(C_5Me_5)_2$ in toluene. The Nb–H link is demonstrated by the infrared ($\bar{\nu}$ 1701 cm^{-1}) and ^{1}H-NMR (13.14) absorptions. Reaction of the "carbene" with hydrogen (1 atm, 25°C) produces Cp_2NbH_3 in 97% yield. This facile reaction has been attributed to oxidative addition of H_2 to a formal 16-electron Nb(III) species, derived from a tautomer of the "carbene," $Cp_2Nb{-}CH_2OZr(H)(C_5Me_5)_2$. $Cp_2W{=}C(H)OZr(H)(C_5Me_5)_2$, which lacks the tautomerization possibility, reacts with H_2 only under more severe conditions and in lower yield (170°C; 50% yield) (*102*).

e. $[CpNb(H)(dmpe)(CO)_2^+]PF_6^-$. The hydrido complexes of niobium that have been characterized generally contain either Cp or chelating phosphine ligands; however, this compound has both. It is made by protonation of $CpNb(dmpe)(CO)_2$ in the presence of the precipitating anion, but the yellow salt is readily deprotonated (*158*).

f. "$CpNbH_2$" *and* "Cp_2NbH_2" *species.* Apart from the salts of the $[Cp_2Nb(H)_2(L)]^+$ cation (L = CO or Pr_3) referred to previously with their nonprotonated $[Cp_2Nb(H)L]$ parents, the only known isolable compound of this type appears to be $CpNb(H)_2(CO)(PPh_3)_2$, whose crystal structure has been reported (*159*). The compound is produced during the photochemical reaction of $CpNb(CO)_2(PPh_3)$ with (Cp). Cp_2NbH_2 and a number of related transient paramagnetic Nb(IV) species have been identified by ESR at −70°C. Photolysis of a benzene/cyclopropane solution containing Cp_2NbH_3 and di-*t*-butyl peroxide at −80°C in the cavity of an ESR spectrometer gives rise to Cp_2NbH_2, and thermal generation of a similar species occurs when isobutylene and Cp_2NbH_3 are mixed in benzene/cyclopropane in a sealed tube at room temperature, yielding $Cp_2Nb(H)(t\text{-butyl})$. Among the other complexes identified by ESR are $Cp(\eta^3\text{-}Cp)Nb(H)_2(allyl)$ and $Cp_2Nb(H)(Cl)$. All these species decompose within a few seconds at 0°C, but their half-lives are of the order of 10 min at −70°C (*160, 161*).

g. Cp_2NbH_3. The initial preparation of this compound involved the high-pressure reaction of H_2 (800 atm) with a toluene solution of niobium pentachloride, cyclopentadienylsodium, and sodium tetrahydroborate (*145*). More recently, it has been prepared by reaction of Cp_2NbCl_2 with a variety of complex hydride reducing agents, such as $LiAlH_4$ and $NaAlH_2(OCH_2CH_2OCH_3)_2$ (Red-al, vitride, etc.) (*147*). The color of the product has been variously reported as white (*145*), yellow (*147*), or brown (*142*), depending on the nature and source of the reducing agent. It appears that the colored materials are contaminated with traces of impurities derived from the reductants.

A mechanism has been proposed for the reactions in which Cp_2NbH_3 is formed from Cp_2NbCl_2 in the presence of hydridoaluminate reducing agents of general formula $[MAlH_2R_2]$ where M is an alkali metal and R is H, Et, or $(OCH_2CH_2OCH_3)$ (*143*). To account for the production of Nb(V) compounds in such circumstances, it is postulated that the initial product is a Nb(IV) hydride, which disproportionates into Nb(V) and Nb(III) hydrides as follows:

$$2Cp_2NbCl_2 + 4MAlH_2R_2 \rightarrow 2Cp_2NbH_2 + 4AlHR_2 + 4MCl$$

$$2Cp_2NbH_2 \rightarrow Cp_2NbH_3 + Cp_2NbH$$

The unsaturated 16-electron Nb(III) species can be trapped in the presence of suitable ligands to give $Cp_2Nb(H)(L)$ complexes, but, in the absence of such additional ligands, it will react with the hydridoaluminum species present in the medium to produce $Cp_2NbH_2AlR_2$ compounds, of which the R = H material has been isolated and partially characterized (the ^{1}H-NMR peak at $\tau = 20$ is assigned to Nb–H–Al bridging hydride). It is interesting that the Nb(V) trihydride is also unstable toward further reaction with the reducing medium, yielding similar compounds via transient $Cp_2NbH_3AlHR_2$ adducts that subsequently lose H_2. However, hydrolysis of $Cp_2NbH_2AlR_2$, whichever way it is formed, quantitatively produces the trihydride, so that the eventual yields of the latter are high. The reaction with $[AlH_2(OCH_2CH_2OCH_3)^-]$ is more complicated than is the case with

(AlH_4^-) or ($AlH_2Et_2^-$). Both the color of the final trihydride and the chemistry of compounds derived from it [e.g., $Cp_2Nb(H)(CO)$] suggest that the product is contaminated with material derived by hydrogen abstraction from carbon adjacent to oxygen in the alkoxy substituents of the reductant, even though this impurity does not show in the ^1H-NMR spectrum (*142*).

^1H-NMR and infrared spectra of the trihydride show absorption at $\tau = 13.72$ and $\tau = 12.73$ and $\bar{\nu} = 1710\ cm^{-1}$, respectively, indicating the presence of M–H linkages. The latter have been directly observed in the X-ray and neutron diffraction study, which has clearly shown the planar character of the central H_3Nb fragment with the three hydrogens essentially equidistant from the metal and the central M–H bond in a bisecting position (*162*). The angle between the "outside" hydride ligands is 126°, in excellent agreement with the 122° predicted by Lauher and Hoffmann in their molecular-orbital study of bent Cp_2ML_m complexes (m = 1, 2, or 3) (*79*).

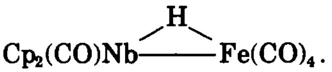
Many of the reactions of this and similar polyhydrides involve elimination of H_2 and the formation of monohydrides. In this respect, the niobium compound turns out to be much more reactive than its tantalum analog (*162*) and readily loses H_2 in the presence of other ligands to form [$Cp_2Nb(H)L$] complexes, as previously described under the appropriate listing for these monohydrides. Reactions with Lewis acids suggest a significantly higher basicity for the unique central M–H bond relative to the other two (*151*). Perhaps the most interesting property is its ability to catalyze H_2/D_2 exchange, possibly via a [Cp_2NbH] intermediate (*145*).

h. $H_5Nb(dmpe)_2$. Reaction of $Me_5Nb(dmpe)$ with H_2 (500 atm) and (dmpe) in THF at 60°C yields the pentahydrido complex as a pale-yellow, waxy, crystalline solid, stable under N_2 for at least several days at room temperature.

A strong, broad peak in the infrared at ~1520 cm^{-1} (Nujol) is assigned to $\bar{\nu}_{M-H}$, and the ^1H-NMR shows a quintet at $\tau = 12.04$ [$^2J(HP) = 39$ Hz], due to the hydrido hydrogens, both in C_6D_6 at 25°C and in toluene-d_8 at −80°C. The ^1H-NMR and ^{31}P-NMR spectra suggest that the barrier to interconversion of idealized structures for [$H_5Nb(dmpe)_2$] in solution is low.

Although $H_5Nb(dmpe)_2$ decomposes upon prolonged standing at room temperature, there is no evidence for the spontaneous and reversible loss of 1 or 2 mol of H_2. However, in the presence of π-acid ligands such as CO, 2 mol H_2 are readily displaced, yielding, e.g., $HNb(dmpe)_2(CO)_2$ as previously mentioned. As with Cp_2TaH_3, the analogous reaction with tantalum is far slower (*140, 141*).

2. *Compounds Containing* Nb–H–M *bridges* (M = *Transition Element*)



$\mathrm{Cp_2(CO)Nb}\overset{\mathrm{H}}{\text{———}}\mathrm{Fe(CO)_4}$

a. $Cp_2(CO)Nb$—H—$Fe(CO)_4$. Addition of a slight excess of $Fe(CO)_5$ and Cp_2NbH_3 in benzene results in an essentially quantitative conversion to $Cp_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$, which can be recovered as air-sensitive dark-brown crystals. The material has been characterized by infrared $\tilde{\nu}_{Nb-H-Fe}$ at 1720 cm^{-1}; ^{1}H-NMR, toluene-d_8, hydride at $\tau = 16.4$; and by X-ray diffraction. It appears to contain both a bridging hydrogen atom and a metal–metal bond. The geometry about niobium can be viewed as a bent sandwich system, analogous to Cp_2NbH_3 with the planar H_3Nb group of the latter replaced by a (H,CO,Fe)Nb moiety (*163, 164*).

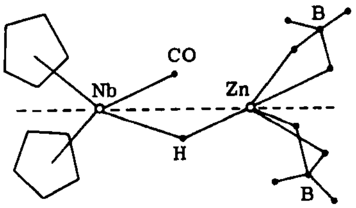
The reaction by which the complex is formed is thought to proceed via a formyl $(HCO)Fe(CO)_4$ species, resulting from an attack of the hydride hydrogen on CO bonded to iron.

b. $Cp_2Nb(H)_2Hf(CH_2Ph)_3$. Reaction of Cp_2NbH_3 with $(PhCH_2)_4Hf$ yields toluene and the binuclear hydrido complex, which decomposes with a half-life of a few hours at room temperature (*151*). No further information on this compound is available.

c. $[Cp_2Nb(H)_2]_2Zn$. This material results from the reaction of Cp_2NbH_3 with Et_2Zn, and its structure has been proposed as involving two mutually staggered, bent Cp_2NbH_2 fragments (analogous to Cp_2NbH_3 without the central H) chelated to the zinc atom, so that the latter has the four hydride hydrogens tetrahedrally disposed about it.

The ^{1}H-NMR (C_6D_6) shows a hydridic resonance at $\tau = 19.05$, and the molecular weight (cryoscopic measurements in benzene) and C,H analyses are consistent with the formula shown (*151*).

d. $Cp_2Nb(CO)(\mu\text{-}H)Zn(BH_4)_2$. Reaction of $NbCl_5$, NaCp, and zinc powder in THF under CO at room temperature followed by treatment with $NaBH_4$ produces yellow crystals of $Cp_2Nb(CO)(\mu\text{-}H)Zn(BH_4)_2$. X-Ray diffraction studies show that the zinc is coordinated to two bidentate BH_4 groups and to niobium via a bent Zn–H–Nb bond and a long direct Zn–Nb linkage (*165*).



3. *Compounds Involving* Nb–H–B *Bonds*

Reduction of Cp_2NbCl_2 with $NaBH_4$ in THF produces dark-green, air-sensitive crystals of $Cp_2Nb(BH_4)$ (*148, 166*). The structure (X-ray) shows bidentate coordination of the BH_4 group (*167*). The room temperature ^1H-NMR spectrum shows an extremely broad multiplet (even after ^{11}B decoupling), and it is clear that, in contrast to the analogous vanadium compound, the bridge-terminal hydrogen exchange process is still rapid even at −90°C (*136*).

a. $Cp_2Nb(BH_4)Cl$. The structure of this poorly characterized material is unknown, and it may well be polymeric (*168*).

b. $Cp_2Nb(CO)(\mu\text{-}H)BF_3$. When BF_3 is added to a solution of $Cp_2Nb(H)(CO)$ in toluene, the red-violet adduct is formed. It is suggested on the basis of infrared and visible spectral data that the BF_3 is coordinated to the hydrido hydrogen (*150*).

4. *Compounds Involving* Nb–H–Al *Bonds*

$Cp_2Nb(L)HAlEt_3$ (L = CO, C_2H_4 or PMe_3), $[(\eta^5\text{-}Cp)(\eta^{1,5}C_5H_4)\text{-}NbHAlEt_3]_2$, $Cp_2NbH_2AlEt_2$, $Cp_2NbH_2AlH_2$, *and* $Cp_2NbH_3AlR_3$ (R_3 = Et_3 or Et_2H). Reaction of Lewis acids such as Et_3Al with niobium hydrido complexes produces air-sensitive, pyrophoric adducts in which the aluminum coordinates to one of the hydride hydrogens. Thus $Cp_2Nb(L)(H)$ compounds (L = CO, C_2H_4, or PMe_3) react to produce the corresponding $Cp_2Nb(L)HAlEt_3$ complexes, which have been identified by their elemental analyses (C,H only), molecular weights (cryoscopically, in freezing benzene; and mass spectrometrically), and ^1H-NMR (C_6D_6, 220 MHz). The latter shows peaks at τ = 21.51, 19.63, and 23.12, respectively, attributable to the hydride ligand in each compound. A similar reaction takes place with "niobocene," yielding $[(\eta^5\text{-}Cp)(\eta^{1,5}\text{-}C_5H_4)NbHAlEt_3]_2$ as a solvate (*151*). $Cp_2NbH_3AlEt_3$ and $Cp_2NbH_3AlHEt_2$ have also been prepared, the former by reaction of the trihydride with Et_3Al (*151*) and the latter from Cp_2NbCl_2 and $NaAlH_2Et_2$ (*142*). ^1H-NMR spectra show peaks at τ = 13.6 and τ = 15.3 for the $AlEt_3$ adduct, and τ = 14.5, 15.0 for the $AlHEt_2$ compound. The monohydrides are stable for at least a week (in solution in benzene) in the dark at room temperature (*151*), but upon standing at room temperature, the trihydride adducts decompose, evolving ethane or hydrogen, respectively, and producing $Cp_2NbH_2AlEt_2$ (*142, 151*).

5. *A Niobium Cluster Hydride*

[$CsNb_6I_{11}H$]. A completely different niobium hydrido species has been reported recently. It apparently contains an octahedral Nb_6 cluster with H at its center; $\bar{\nu}_{Nb-H}$ for this compound is at 1120 cm^{-1} (*169*).

C. TANTALUM HYDRIDE COMPOUNDS

Niobium and tantalum chemistries are frequently very similar, and it is not surprising to find close parallels in their hydrides with respect to which compounds are known and to their properties. However, the two sets of compounds have frequently been discovered by independent workers with different objectives, and this is reflected in the current status of our knowledge of the hydrides.

The comments at the beginning of the niobium section with respect to co-ligands, etc., are equally relevant to tantalum, and most of the niobium hydrides have tantalum analogs, although, as yet, no $Ta-(H)_n-BH_{4-n}$ compounds have been reported. Terminal tantalum–hydrogen bonds are usually characterized by $\bar{\nu}_{Ta-H}$ infrared absorption in the region ~1600–1800 cm^{-1}, though, as with niobium, the (dmpe) hydride absorptions are somewhat lower (~1550–1650 cm^{-1}). The ^1H-NMR spectra show absorptions in the range $\tau = 10-20$, depending on the compound. Details are provided in Table VI. The order of discussion is the same as that for niobium.

The emphasis in the treatment that follows is on compounds that can be isolated, and the transient tantalum hydride species postulated in, for example, the work of Schrock *et al.* on alkylidenes (*184, 194*) are only briefly mentioned. The subject of metal hydride formation during hydrogen elimination reactions is worth a review in its own right, and indeed several exist. One of the most recent deals primarily with osmium hydrides and alkyls but is relevant to tantalum also (*195*). It can be consulted for other references, and the subject is not treated further here.

1. $HTa(dmpe)_2(L)_n$ *Complexes and Related Species*

a. $HTa(dmpe)_2(CO)_2$ *and related cations.* The orange neutral compound is made from the pentahydride by reaction with CO at 1500 psi (in benzene at 80°C) (*171*), and it has also been identified as an intermediate in the reaction in which [$(dmpe)_2Ta(CO)_2X$] compounds (X = Cl, Br, Me, CN) are produced from [$(dmpe)_2Ta(CO)_2$]$^-$ by treatment

TABLE VI

TANTALUM HYDRIDE COMPLEXES

Compound	Preparation	Properties	^1H NMR (τ, M–H)	Infrared (cm^{-1})	Comments	References
$HTa(CO)_2(dmpe)_2$	(a) $TaCl_5/K/H_2/dmpe$, then (2) + CO (in benzene) (b) $TaCl_5(dmpe)$ + (1)CO then (2)Na/Hg and (3)H^+	Orange crystals, M.P. 140–141°C.	14.17 triplet of triplets (8°C); $^2J(^1H-^{31}P)$ 14.25, 89.25 Hz.	$\bar{\nu}_{C-O}$ 1737 $\bar{\nu}_{Ta-H}$ 1589	X-Ray; ^{31}P NMR; mass spectrum.	*171–173*
$HTa(PPh_2)_2(dmpe)_2$	$TaCl_2(dmpe)_2/KPPh_2/THF$/0°C	Purple crystals.	Not found.	$\bar{\nu}_{Ta-H}$ 1648	X-Ray; ^{31}P NMR; mass spectrum.	*174*
$HTa(\eta^4-C_{10}H_8)(dmpe)_2$	$[Ta(\eta^4-C_{10}H_8)(dmpe)_2]^- + H^+$	Orange crystals.	10.23 (toluene-d_8, 25°C)		X-Ray of Cl-compd.; ^{31}P NMR; mass spectrum.	*175*
$Cp_2Ta(H)(CO)$	(a) $Cp_2Ta(H)(alkene)/CO$ (b) Cp_2TaH_3/CO/toluene	Purple crystals.	16.75 or 16.80, 5.50 (Cp)	$\bar{\nu}_{C-O}$ 1885		*145, 176*
$Cp_2Ta(H)(alkene)$	(a) $Cp_2TaCl_2/RMgCl$(ether) R = n-$C_3H_7 \rightarrow C_3H_6$ complex n-$C_4H_9 \rightarrow C_4H_8$ complex n-$C_5H_{11} \rightarrow C_5H_{10}$ complex $C_5H_9 \rightarrow C_5H_8$ complex (b) $Cp_2Ta(CHMe)(Me)$/heat	Yellow → purple (depending on alkene).	13 → 13.6, depending on alkene and whether *endo* or *exo* isomer.	$\bar{\nu}_{Ta-H}$ 1750–1800; $\bar{\nu}_{C-C}$ ~1450; $\bar{\nu}_{Ta-H}$ 1570.	^{13}C NMR	*146, 177*
$Cp^*_2Ta(H)(alkyne)$ ($Cp^* = C_5H_4Me$)	(a) $Cp^*_2TaH_3$/alkyne (b) $Cp^*_2TaH_3$/alkyne/ iodobenzene, then $LiAlH_4$ alkynes: $[(n-C_3H_7)_2C_2]$; $MeC_2(n-C_2H_9)$; $MeC_2(t-C_4H_9)$; $MeC_2(i-C_3H_7)$		10.2 for $(n-C_3H_7)_2C_2$.	$\bar{\nu}_{Ta-H}$ 1800; $\bar{\nu}_{Ta-D}$ 1275; $\bar{\nu}_{C-C}$ 1770.		*178*
$Cp_2Ta(H)(PEt_3)$	(a) Cp_2TaH_3/PEt_3 (b) $Cp_2Ta(H)(alkene)/PEt_3$	Red crystals.	19.48 or 19.56; $^2J(^1H-^{31}P)$ 21 Hz; 5.68 (Cp).	$\bar{\nu}_{Ta-H}$ 1705		*146, 179*
$[(Cp)(\eta^{1,5}-C_5H_4)Ta(H)]_2$	Cp_2TaH_3/heat				Similar spectral properties to "niobecene" dimer.	*145*
$[Cp'Ta(H)(Cl)_2]_2$ ($Cp' = C_5Me_4R$)	$Cp'Ta(propylene)(Cl)_2/H_2$ (40 psi, 25°C, pentane)	Green crystals.	20.45	$\bar{\nu}_{Ta-H}$ 1585 $\bar{\nu}_{Ta-D}$ 1150	Diamagnetic	*180*
$Cp'_2Ta_2(H)(Cl)_4(HCO)$	$[Cp'Ta(H)(Cl_2)]_2$/CO/0°C	Orange crystals.	17.52		^{13}C NMR	*180*
$Cp'_2Ta_2(H)(Cl)_4(HCO)(PMe_3)$	Previous compound/PMe_3	Yellow crystals.	20		X-Ray; ^{13}C NMR.	*180*

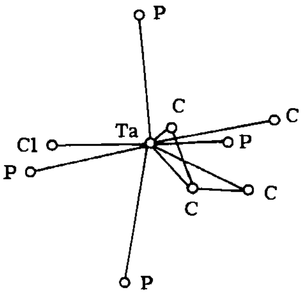
[$Cp_2Ta(H)Li$] ?	$Cp_2TaH_3/Li(n\text{-}Bu)$	Orange yellow crystals, not fully characterized.		$\tilde{\nu}_{Ta-H}$ 1590		*181, 182*
[$CpTa(H)(Me)_3$] ?	$Ta(Me)_3Cl_2/Cp_2Pb$	Air-sensitive yellow crystals.				*183*
$Cp^*Ta(H)(Me)_2(OCHMe_2)$	$Cp^*Ta(Me)_4/CO/H_2$	Not isolated.	Not located.	$\tilde{\nu}_{Ta-H}$ 1730		*184*
CpTaH		Intermediates in numerous reactions especially decomposition of Ta alkyls, etc.				*185–187*
$Cp_2Ta(H)_2(SnMe_3)$	Cp_2TaH_3/Me_3SnNMe_2	White crystals, m.p. 154–156°C.	14.63 (benzene-d_6); 5.53 (Cp).	$\tilde{\nu}_{Ta-H}$ 1750		*188*
$Cp_2Ta(H)_2$	Cp_2TaH_3 photolysis in presence of di-*t*-butyl peroxide.	Paramagnetic intermediates identified by ESR. Not isolable, although Me_2 analogs are.			ESR	*160*
Cp_2TaH_3	(a) $Cp_2TaCl_2/NaAlH_2(OR)_2$ (b) $TaCl_5/NaCp/NaBH_4$	White crystals; m.p. 187–189°C (dec.).	11.63 triplet; 13.02 doublet (benzene-d_6).	$\tilde{\nu}_{Ta-H}$ 1735	X-Ray and neutron diffraction P.E.S.; mass spectrum.	*162, 181, 182, 188–190*
$Cp^*_2TaH_3$ ($Cp^* = C_5H_4Me$)	$TaCl_5/LiCp^*/LiAlH_4$	White crystals, m.p. 89.5–91°C.	10.69 (triplet); 12.20 (doublet).	$\tilde{\nu}_{Ta-H}$ 1740		*191*
$H_5Ta(dmpe)_2$	(a) $TaCl_5/K/H_2$/dmpe/benzene (b) $Me_5Ta(dmpe)/H_2$/dmpe/THF	Air-sensitive white crystals.	10.70 quintet; $^2J(^1H-^{31}P)$ 35 Hz.	$\tilde{\nu}_{Ta-H}$ 1544 (Nujol)	Mol. weight (cryoscopy)	*140, 141, 171*
$Cp_2Ta(CO)(\mu\text{-}H)Fe(CO)_4$	$Cp_2TaH_3/Fe(CO)_5$		16.70		Crystal structure of Nb analog.	*164*
$(\mu\text{-}H)_2\text{-}(\mu\text{-}Cl)_2[Ta(PMe_3)_2Cl_2]_2$	(a) $TaCl_5$ + Na/Hg + PMe_3 (b) H_2	Green crystals	Complex multiplet centered at 18.5 attributed to Ta–H–Ta bridging hydrides.	No bands attributable to Ta–H–Ta	X-Ray structure mol weight; ^{31}P NMR.	*199*
$Cp_2TaH_3 \cdot L$	Cp_2TaH_3 + Lewis acids (L) at low temperature (L = $AlEt_3$, $GaEt_3$, $ZnEt_2$, $CdEt_2$)	Strong adducts undissociated in freezing benzene.	14.68 and 12.46 (benzene-d_6); L = $AlEt_3$.		Mol. weights (cryoscopy)	*151*
{$Ta[H_3Al(OR)_2](dmpe)_2$}$_2$ (R = —$CH_2CH_2OCH_3$)	$TaCl_2(dmpe)_2/Na[AlH_2(OR)_2]$		16.30	$\tilde{\nu}_{Ta-H}$ 1605, 1640	^1H NMR of τ_{TaH} unchanged between +90 and −70°C; crystal structure (X-ray).	*192*
$Ta(AlH_4)_4$?	$TaCl_5/LiAlH_4$/ether	A variety of poorly characterized products.				*193*
[$Ta(HC)CMe_3(PMe_3)Cl_3$]$_2$	$Ta(CH_2CMe_3)_2Cl_3$ + PMe_3(toluene)/24 h/25°C	Red nuggets			X-Ray structure showing Ta–H–C interaction.	*200*

with HCl, HBr, CH_3I, and HCN, respectively (*172*). Crystal and solution structures have been determined by X-ray diffraction and NMR (^1H and ^{31}P) studies, respectively (*173*). The solid contains a seven-coordinate hydride-capped distorted octahedron, and a similar structure is indicated in solution below 0°C; however, above this temperature the compound is fluxional. A detailed analysis of the temperature-dependent line shape for the hydride region of the ^{1}H-NMR spectra (90 and 220 MHz) indicates that a second isomer is present in low concentration. The infrared spectrum (C_6D_6) shows $\bar{\nu}_{Ta-H}$ at 1589 cm^{-1} and $\bar{\nu}_{C-O}$ at 1737 cm^{-1}.

$HTa(dmpe)_2(CO)_2$ has been the subject of two recent independent cyclic voltammetry studies (*196, 197*). Reversible oxidation to $[HTa(dmpe)_2(CO)_2]^+$ was observed in both cases, but the cation seems more stable in acetonitrile (*197*) than in acetone (*196*). An irreversible oxidation to an unstable dication occurred in either solvent at more positive oxidizing potentials. There is no evidence to suggest that the 17-electron monocations are stable for long enough to be isolated, nor is there any indication that they can be produced by chemical oxidation (*196*).

b. $HTa(dmpe)_2(PPh_2)_2$. This purple compound results from the stoichiometric reaction of $Ta(dmpe)_2Cl_2$ and $K(PPh_2)$ in THF (0°C) with, presumably, proton abstraction from the solvent. The infrared $\bar{\nu}_{Ta-H}$ is at 1648 cm^{-1}, and mass spectral evidence for the hydride was also conclusive. Although an X-ray study did not locate the hydride, its position was revealed by the dispositions of the other ligands. The structure is that of a pentagonal bypyramid with the PPh_2 groups occupying apical positions. For Ta–H, a value of τ was not found in the ^{1}H-NMR spectrum (*174*).

c. $HTa(dmpe)_2(\eta^4\text{-}C_{10}H_8)$. This orange crystalline material has been isolated from the reaction of $TaCl_4(dmpe)_2$ with excess sodium naphthalene followed by protonation with cyclohexanol. It shows a



characteristic ^{1}H-NMR hydride peak at $\tau = 10.23$, compared to $\tau = 14.17$ for the carbonyl hydride $HTa(dmpe)_2(CO)_2$ (*175*). Although its structure is not known directly, that of $ClTa(dmpe)_2(\eta^4\text{-}C_{10}H_8)$ involves an approximately pentagonal bypyramidal geometry about tantalum. The structural parameters of the chloro complex indicate considerable π-acceptor interaction by the diene portion of the arene, which may well explain the substitutional inertness of the Ta–naphthalene unit as demonstrated by the noncatalysis of D_2/C_6H_6 exchange by $HTa(dmpe)_2(\eta^4\text{-}C_{10}H_8)$ in contrast to the catalytic behavior of $H_5Ta(dmpe)_2$ or by other η^4-arene complexes. A very stable $Ta\text{–}(\eta^4\text{-}C_{10}H_8)$ bond is indicated (*175*).

2. [$Cp_2Ta(H)L$] *Complexes*

Compounds of this general formula are known where L = CO (*145, 176*), various alkenes (*146, 177*) and alkynes (*178*), and also PEt_3 (*146, 179*). In addition, a tantalum analog of "niobocene" has been reported (*145*).

a. $Cp_2Ta(H)(CO)$. This complex is made by reacting the trihydride, Cp_2TaH_3, with CO at high pressure (*145*), but a more convenient route is the conversion of the corresponding monohydride alkene complexes using CO at 1 atm (70°C, toluene) (*176*). The purple compound shows $\bar{\nu}_{Ta-H}$ at 1750 cm^{-1} and a ^{1}H-NMR resonance attributable to hydride at $\tau = 16.80$.

b. $Cp_2Ta(H)$(alkene). Treatment of Cp_2TaCl_2 with RMgCl (R = $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, or C_5H_9) gives the corresponding tantalum hydride π-olefin complexes $Cp_2Ta(H)$(alkene) (alkene = C_3H_6, C_4H_8, C_5H_{10}, and C_5H_8) (*146*). In the C_3H_6 case, two isomers occur. $Cp_2Ta(H)$(propylene) can be produced in fair yield from the thermal decomposition of $Cp_2Ta(CHMe)(Me)$ (*177*). Both *exo* and *endo* isomers are present, though it seems likely that the former is the initial product. The materials show infrared $\bar{\nu}_{Ta-H}$ absorption in the range 1750–1800 cm^{-1}, and ^{1}H-NMR peaks due to hydride hydrogen in the region $\tau = 13.05$ to 13.68 depending upon the alkene. They are thermally stable (to 100°C) and sublimable (e.g., C_3H_6 complex, 95°C, 10^{-2} mmHg) and may be readily converted into other tantalum hydride species by displacement of the alkene in the presence of other ligands. For example, H_2 (1 atm, 90°C, toluene solution) yields Cp_2TaH_3, and PEt_3 (90°C, toluene) gives $Cp_2Ta(H)(PEt_3)$. Both reactions are quite slow, requiring about 14 h for completion. Reaction with CO is more complicated, in that either alkene or hydride ligands may be displaced. In the latter case, the products are of the form $Cp_2Ta(CO)R$, presumably due to the migration of the hydride onto the alkene. These alkyl carbonyl complexes show remarkable thermal stability, compared to other early transition metal alkyls, with decomposition only occurring above 150°C (*146*). A reaction seemingly analogous to the hydride displacement by CO occurs with aryl or alkyl isocyanides. *Endo*-$Cp_2Ta(H)(C_3H_6)$ and $Cp_2Ta(H)(C_4H_8)$ are converted into the adducts $Cp_2Ta(C_3H_7)(R'NC)$ and $Cp_2Ta(C_4H_9)(R'NC)$, respectively (*198*).

c. $[Cp^*_2Ta(H)(alkyne)]$ ($Cp^* = \eta^5$-C_5H_4Me; alkyne, $RC{\equiv}RR'$; $R = CH_3$; $R' = n$-C_3H_9, i-C_3H_7, or t-C_4H_9; $R + R' = n$-C_3H_7). Refluxing $Cp^*_2TaH_3$ with the appropriate acetylene in toluene leads to the slow formation of these monohydrido complexes (*178*). However, they are more readily obtained, in high yield, via the monoiodo compounds (*178*).

$$Cp^*_2TaH_3 + \text{alkyne} + \text{iodobenzene} \xrightarrow[\text{dioxane}]{\text{reflux}} Cp^*_2Ta(I)(\text{alkyne})$$

$$Cp^*_2Ta(I)(\text{alkyne}) \xrightarrow[Et_2O]{LiAlH_4} Cp^*_2Ta(H)(\text{alkyne})$$

The hydrides show $\bar{\nu}_{Ta-H}$ (infrared) bands around 1800 cm^{-1} (1275 cm^{-1} for the deuteride) and ^{1}H-NMR hydride absorption at $\tau = 10.2$.

Reaction of the oct-4-yne complex with HBF_4 liberates *cis*-oct-4-ene, and this is postulated as occurring via initial protonation of the metal (to yield $[Cp^*_2Ta(H)_2(alkyne)]^+$), followed by insertion of acetylene into the Ta–H bond and C–H reductive elimination. *cis*-Oct-4-ene also results when H_2 is reacted with the hydrido complex at 100°C (*178*).

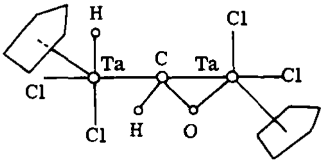
d. $Cp_2Ta(H)(PEt_3)$. Tebbe first made this compound by reacting Cp_2TaH_3 with PEt_3 (*179*), but an easier route employs $[Cp_2Ta(H)(alkene)]$ as described above (*146*). The red crystalline material shows ^{1}H-NMR absorption at $\tau = 19.48$ (hydride) and $\bar{\nu}_{Ta-H}$ (infrared) at 1705 cm^{-1} but has not been otherwise characterized.

e. $[HTa(\eta^5$-$Cp)(\eta^{1,5}$-$C_5H_4)]_2$. Refluxing Cp_2TaH_3 in benzene produces "tantalocene," whose properties and structure are similar to those of its niobium analog (*145*).

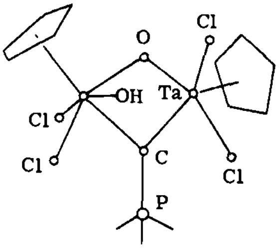
3. (C_5Me_4R)Ta(H)Cl_2 *and Related Compounds*

Reaction of H_2 (40 psi, 25°C, pentane) with $(C_5Me_4R)Ta(propylene)Cl_2$ produces a green diamagnetic material of stoichiometry $[(C_5Me_4R)Ta(H)Cl_2]_2$ (**XL**) showing $\bar{\nu}$ (infrared) at 1585 cm^{-1}, which moves to 1150 cm^{-1} upon deuteration, and which is presumably $\bar{\nu}_{Ta-H}$.

The ^{1}H-NMR reveals a peak at $\tau = 20.45$, attributable to Ta–H. The structures of these compounds probably contain a metal–metal single bond supported by two bridging M–H–M bonds. This reaction occurs for various R(alkyl) groups, but when R is Et the green product reacts with CO at 0°C yielding an orange compound of apparent composition $[(C_5Me_4Et)Ta(H)Cl_2]_2(CO)$ (XLI). However, from the ^{1}H- and ^{13}C-NMR spectra, its structure contains only one H–Ta bond, with the other hydrogen attached to carbon, in the unique manner shown below (i.e., an η^2-formyl complex).



This material reacts with PMe_3, forming an adduct (**XLII**) whose structure (from X-ray data) is shown below.



The ^{1}H-NMR spectra of these latter compounds (**XLI**) and (**XLII**) show τ_{Ta-H} at 17.52 and 20, respectively (*180*).

Compound (XL) can also be produced from $(C_5Me_4R)Ta(CH_2CMe_3)_2Cl_2$ and H_2. A co-product in this reaction is red $(C_5Me_4R)_2Ta_2(H)Cl_5$, which is assumed to contain one Ta–H–Ta bridge bond. This material reacts with CO to form a complex similar to (**XLI**) but with the terminal H replaced by Cl (*180*). There is good evidence that simple formyl complexes are unstable with respect to CO–M–H rearrangement, so that compound (**XLI**) presumably owes its existence to the "stabilization" of the formyl ligand by coordination to a second metal (Lewis acid) (*180*).

4. *Other* "CpTa(H)" *Systems*

Green has isolated an orange-yellow material from the reaction of Cp_2TaH_3 with *n*-butyllithium in toluene, which, although not fully characterized, appears to contain the $Cp_2Ta(H)$ grouping ($\tilde{\nu}_{Ta-H}$ 1590 cm^{-1}) and also a Ta–Li bond. It is, perhaps, analogous to $[Cp_2W(H)Li]_4$ (*181, 182*). An air-sensitive yellow compound believed to be $CpTa(H)(Me)_3$ has been reported by Holliday *et al.,* but has not been characterized. It is a co-product of the reaction between Cp_2Pb and $TaMe_3Cl_2$ (*183*). An apparently similar compound, $Cp^*Ta(H)(Me)_2(OCHMe_2)$, with $\tilde{\nu}_{Ta-H}$ at 1730 cm^{-1}, has recently been reported. It is an unisolated product of the reaction of $Cp^*Ta(Me)_4$ with, successively, CO and H_2 (*194*). CpTa(H) moieties have been proposed as intermediates in numerous catalytic reactions. These are assumed to result from hydrogen abstractions (*185–187*).

a. $Cp_2Ta(H)_2(SnMe_3)$. Dimethylamine trimethylstannane provides a convenient route to metal–metal bonds involving tin, and stoichiometric reaction of this compound with Cp_2TaH_3 in THF (reflux, 6 h) affords the white crystalline $Cp_2Ta(H)_2(SnMe_3)$ with concommittant release of amine (*188*).

The dihydrido complex melts without decomposition (154–156°C). It shows a hydrido absorption (^{1}H-NMR) at $\tau = 14.63$ and $\tilde{\nu}_{Ta-H}$ 1750 cm^{-1}.

b. Cp_2TaH_2. Like its niobium analog, this compound has been identified by ESR studies of photolytic reactions of Cp_2TaH_3 with di-*tert*-butyl peroxide. It was not isolated, although the corresponding $Cp_2Ta(Me)_2$ was (*160*).

c. Cp_2TaH_3 *and* $(C_5H_4Me)_2TaH_3$. The Cp_2 compound can be made by reaction of Cp_2TaCl_2 with $NaAlH_2(OCH_2CH_2OCH_3)_2$ (*182*), or from $TaCl_5$, NaCp, and $NaBH_4$ (*181*). The substituted Cp complex is made from $TaCl_5$, $Li(MeC_5H_4)$, and $LiAlH_4$ (*191*). ^{1}H-NMR studies show two resonances attributable to the hydrido hydrogen; in the Cp_2 compound these occur at 11.63 (triplet) and 13.02 (doublet), while they are at 10.69 (triplet) and 12.20 (doublet) in the other complex (*188, 191*); $\tilde{\nu}_{Ta-H}$ (infrared) is at 1735 and 1740 cm^{-1}, respectively.

The crystal structure of Cp_2TaH_3 has been determined by X-ray and neutron diffraction methods; it is isostructural with Cp_2NbH_3 (*162*). Photoelectron spectra show the relationships between $Cp_2Re(H)$, Cp_2WH_2, and Cp_2TaH_3; the varying number of lone pairs on the respective metals (2, 1, and 0) are particularly clearly indicated (*189*). The relationships between such hydrides have also been studied mass spectrometrically (*190*). The preponderance of (Cp_2TaH^+) ions over (Cp_2Ta^+), in contrast to the reverse situation for Cp_2MoH_2, is noteworthy. Clearly, the unique central M–H bond of the H_3M moiety is stronger than the other two, consistent with the reactions of Cp_2TaH_3 and its niobium analog.

The catalytic behavior of Cp_2TaH_3 and $(C_5H_4Me)_2TaH_3$ with respect to benzene–D_2 exchange has been studied. Not only do these compounds show much slower rates of exchange than Cp_2NbH_3, but they also do not discriminate among various substituted benzene substrates, while the niobium compound does. Possible reasons for these differences have been discussed in terms of a mechanism involving a series of alternating reductive-elimination and oxidative-addition steps (*191*).

d. $H_5Ta(dmpe)_2$. This pentahydrido complex can be made from $TaCl_5$ or $(TaPh_6^-)$, H_2 (1500 psi), and (dmpe). In the former case, potassium is also needed, and the reaction is done in benzene as opposed to THF for the hexaphenyl route. The latter is slightly more facile (45°C, 5 h, compared to 115°C, overnight) (*171*). The pentahydride can also be produced from its pentamethyl analog by reaction with H_2 (500 atm, 60°C in THF) in the presence of excess (dmpe) (*140, 141*). In each case, the air-sensitive product is white and crystalline, melting with decomposition at 133–135°C. The infrared (Nujol) $\tilde{\nu}_{Ta-H}$ occurs at 1544 cm^{-1}, and the ^{1}H-NMR (toluene-d_8) hydride absorption is a quintent at $\tau = 10.70$. The compound appears to be fluxional down to at least −140°C (*171*). Hydride ligands are readily displaced leading to monohydrido complexes as already discussed, and D_2/benzene exchange is catalyzed by a mechanism that almost certainly involves interconversions like

$$H_5M \xrightarrow{-2H_2} HM \xrightarrow{+2H_2} H_5M$$

5. *Compounds Involving* Ta–H–M *Bridges*

M is a transition element, and the only compounds to mention here are $Cp_2(CO)Ta(H)Fe(CO)_4$, which is produced in a fashion analogous to the niobium compound and has a similar structure (*164*), and the very unusual $(\mu\text{-}H)_2\text{-}(\mu\text{-}Cl)_2$-ditantalum species $[Ta_2Cl_6(PMe_3)_4H_2]$, whose X-ray structure has recently been determined (*199*). The bridging hydrogens were not directly located, but their positions were clearly indicated by the disposition of the other atoms, and they were identified in a 360 MHz ^{1}H-NMR study.

6. Ta–H–Al *Bridges*

a. $Cp_2TaH_3AlEt_3$ *and related compounds.* Reaction of Cp_2TaH_3 with Et_3Al produces a bridge-bonded adduct similar to the niobium compound. ^{1}H-NMR absorptions due to the hydride hydrogens occur at $\tau = 12.46$ and 14.68.

Similar adducts are formed with $GaEt_3$, $ZnEt_2$, and $CdEt_2$. These compounds are more stable than their niobium counterparts (*151*).

b. $(dmpe)_2Ta[H_2Al(OCH_2CH_2OCH_3)_2]$. This compound, in which Ta–H–Al linkages are implied (infrared $\tilde{\nu}$ 1605 and 1640 cm^{-1}; $\tau = 16.30$, ^{1}H-NMR) can be isolated from the reaction of $TaCl_2(dmpe)_2$ with $Na[H_2Al(OCH_2CH_2OCH_3)_2]$. The crystal structure has been determined by X-ray diffraction methods, but the bridging hydrogens were not located (*192*).

c. $[H_nTa(AlH_4)_{4-n}]$ $(n = 0–4)$. Compounds of this general formula apparently occur in the reaction products from reduction of $TaCl_5$ by $LiAlH_4$ (in Et_2O). They do not appear to have been characterized (*193*).

7. *A* Ta–H–C *Bridge?*

A neutron diffraction study of $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ has revealed an interaction between Ta and H of the adjacent (CH) group, which may be considered as a Ta–H–C linkage. The importance of such an interaction in facilitating removal of the α hydrogen (e.g., by an alkyl ligand to give an alkane) was noted (*200*).

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