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Advances in the chemistry of bis-cyclopentadienyl hydride derivatives of niobium and tantalum

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Abstract

The bis-cyclopentadienyl hydride chemistry of the elements niobium and tantalum has been dominated by the family of trihydride complexes, namely Cp_2MH_3 (M = Nb, Ta, Cp = C_5H_5, C_5Me_5, $C_5H_4SiMe_3$, $C_5H_3(SiMe_3)_2$ and related substituted cyclopentadienyl rings). The chemical and spectroscopic properties of these complexes are strongly influenced by both the nature of the Cp ring and the metal center. In some cases, anomalous NMR spectroscopic behavior has been observed, and values of J_{HH} that are largely dependent on the temperature have been found. This behavior can be modulated by means of the interaction of the trihydride complexes with Group 11 metal fragments, and in some cases HH interactions in the molecules can be observed. Several X-ray crystal structure determinations of this kind of complex, as well as different theoretical calculations, have been performed in order to gain a deeper insight into these systems. The reactivity of the trihydride metallocene complexes has been extensively considered. Thus, the easy elimination of H_2 from the Cp_2MH_3 species, giving rise to the unsaturated species Cp_2MH, has been used to study the activation processes of several kinds of H–X bond, in hydrosilanes, hydrogermananes, etc., which allows the synthesis of complexes such as Cp_2MH_2X. This type of complex has been extensively studied, especially when X = SiR_3, because in several cases these complexes exhibit a special hypervalence behavior. A large family of complexes of stoichiometry Cp_2MHL was prepared from the reaction of the Cp_2MH_3 complexes with different classes of π-acid ligands, L. The Cp_2MHL complexes can undergo insertion reactions into the M–H bond with several classes of unsaturated molecules, and such processes are of interest in the field of organic synthesis. Furthermore, the protonation processes of the Cp_2MHL complexes give rise to a new family of η^2-H_2-containing cationic species, $Cp_2M(\eta^2\text{-}H_2)L^+$, which are stable at low temperatures. The NMR data of such compounds indicate that it is possible to block the rotation of the H_2 molecule at low temperatures. Of particular interest are the Cp_2MH(olefin) complexes, and these have been widely studied because they can be considered as excellent models for the study of the β-elimination reaction and the reverse olefin insertion process. Finally, from the trihydride derivatives Cp_2MH_3 and related species, several heterometallic complexes have been prepared and characterized.

Keywords: Niobocene; Tantalocene; Hydride; Cyclopentadienyl; Synthesis; Reactivity

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1. Introduction

Hydride complexes of transition metals represent one of the most important classes of compounds because of their chemical reactivity and their important role as intermediates in a number of catalytic hydrogenation processes [1]. This review is concerned with both the spectroscopic and chemical behavior of bis-cyclopentadienyl hydride complexes of niobium and tantalum since they constitute a special family of hydride-containing organometallics of early transition metals [2]. Bis-cyclopentadienyl niobium or tantalum hydride derivatives have long been of interest for both their high reactivity and their spectroscopic properties. In particular, the spectroscopic properties of the niobocene and tantalocene trihydrides, namely

Cp_2MH_3 (M = Nb, Ta, Cp = C_5H_5, C_5Me_5, $C_5H_4(SiMe_3)$, $C_5H_3(SiMe_3)_2$, etc.), are of great interest. Thus, bis(cyclopentadienyl)niobium trihydrides exhibit quantum mechanical exchange couplings, and this phenomenon, also observed with other transition metal complexes, is characterized by the presence of large temperature-dependent H–H coupling between the hydrides. Nevertheless, the analogous tantalocene trihydrides exhibit the behavior of classical hydrides. A rich chemistry of hydride complexes has been developed from studies of the reactivity of the trihydride complexes Cp_2MH_3 towards several types of reagents. Thus, an extensive family of 18-electron niobium (III) and tantalum (III) hydrides, Cp_2MHL, has been reported from the reactions of the trihydride complexes with π-acid ligands, namely phosphine, phosphite, olefin, isocyanide, etc. Some of these complexes are of special interest; for example, the bis(cyclopentadienyl)–hydride–olefin species are among the more interesting hydride–olefin complexes and they are especially appropriate for the study of the insertion of olefins into metal–hydride bonds and its microscopic reverse, beta-elimination, which are very common steps in industrial catalytic reactions such as olefinic isomerization, hydrogenation, and hydroformylation [3]. Furthermore, the discovery by Kubas [4] of dihydrogen coordination on a transition metal center has led to intense research activity in the chemical, theoretical, and spectroscopic aspects of the synthesis of dihydrogen complexes. As a consequence, it has been possible to easily carry out the synthesis of Group 5 dihydrogen complexes, $Cp_2M(\eta^2\text{-}H_2)L^+$ [5], by protonation at low temperature of monohydride complexes, Cp_2MHL. These complexes also exhibit interesting spectroscopic properties. The oxidative addition of organo-Group 14 element hydrides to coordinatively unsaturated niobium or tantalum hydride complexes has also been applied to the preparation of interesting Group 14 fragments containing niobium or tantalum organometallics. The reactivity of these compounds has been widely studied. In other fields, insertion processes of unsaturated molecules, such as carbon disulfide, carbon dioxide, alkynes, heterocumulenes etc., into the hydride niobium and tantalum bond, which constitute fundamental chemical steps in several catalytic cycles and frequently lead to reactive intermediates [3b], have been considered. Finally, in another interesting aspect of the reactivity, the selective substitution of protons in the coordination sphere of niobium or tantalum hydride complexes by metallic fragments occurred. This gave rise to the synthesis of a series of heterometallic hydride species associating several transition metals and Group 5 metals.

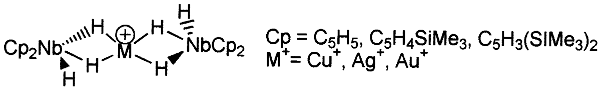
This review will summarize, in a comprehensive fashion, the synthesis, characterization, structure and reactivity of bis-cyclopentadienyl hydride complexes of niobium and tantalum. Certain areas, however, have received a good deal more attention than others for various reasons, and in these cases we have tended to adhere to the pattern of the original studies. Coverage of the literature is up to the middle of 1998.

2. Hydrogen exchange coupling in metallocene trihydride complexes

The trihydride niobocene or tantalocene complexes, Cp_2MH_3 (M = Nb, Ta,

$Cp = C_5H_5$, C_5Me_5, $C_5H_4(SiMe_3)$, $C_5H_3(SiMe_3)_2$ and related substituted cyclopentadienyl rings), are probably the most useful starting materials in the bis-cyclopentadienyl hydride chemistry of these elements. References to various preparations of these compounds and selected references for their use in synthesis can be found within Ref. [2] of this review. In particular, the preparation of niobium trihydride containing silylated cyclopentadienyl rings has been described [6] using the reaction of Cp'_2NbCl_2 or Cp'_2NbCl_2 ($Cp' = C_5H_4SiMe_3$, $Cp' = C_5H_3(SiMe_3)_2$) with $NaAlH_2(OCH_2CH_2OMe)_2$ ('Red-Al'). This method, i.e. the reaction of a dichloride metallocene of niobium or tantalum with an excess of a hydride-containing aluminum reagent, has been widely employed for the synthesis of metallocene trihydride complexes. The properties of the niobocene trihydride, Cp_2NbH_3, have been of great interest ever since Parshall and Tebbe [7] demonstrated its activation of carbon–hydrogen bonds. In particular, the ^1H NMR properties of this complex have been found to be anomalous in many respects. The first study reported that the hydride gave two separate broad resonances at room temperature (r.t.), which sharpened at low temperature [8]. Subsequently, Curtis et al. observed a small temperature-dependence of the coupling constant $J(H,H)$ of the hydrido hydrogen that was not explained [9]. Similarly, the adduct of Cp_2NbH_3 with $AlEt_3$ exhibits a surprisingly large value of $J(H,H)$ [8]. This anomalous behavior was found to be due to a phenomenon of hydrogen exchange coupling 20 years ago, a situation that is present in several trihydrides of Ru [10], Ir [11], Nb [6,12], Os [13] and Mo [12], all of which adopt the same geometry, implying a planar array for the three hydrides and the metal. Exchange coupling between only two hydrides has been observed in a tantalum dihydride [14]. The quantum mechanical nature of the coupling was recognized by Zilm [15] and Weitekamp [16], who proposed the existence in these compounds of exchange coupling between two hydrogen atoms. Exchange couplings are known in EPR, but their observation in 'heavy' particles such as protons was novel in coordination chemistry. Heinekey [12] has analyzed the effect of the exchange coupling in the metallocene trihydride complexes Cp_2MH_3 ($M = Nb$, Ta; $Cp = C_5H_5$) by ^1H NMR spectroscopy. In this study, moderate values of the J_{A-B} coupling were observed at r.t., a fact consistent with an AB_2 spin system for the hydride ligands. The Ta complex exhibits a proton coupling of 9.5 Hz, which is independent of the temperature in the range 203–303 K. Therefore, no significant exchange coupling was found in this metallocene. Conversely, for the Nb complex, a clear temperature dependence is found for the observed coupling that decreases with decreasing temperature, practically vanishes at 243 K and then reappears at 173 K. This phenomenon was attributed to a modest quantum mechanical exchange coupling, which is a sensitive function of temperature, that has a value of 26.4 Hz at 303 K and a value of zero at 173 K. In these complexes that exhibit hydrogen exchange coupling, the observed constant, J_{obs}, is given by the relationship $J_{obs} = -2J_{exch} + J_{magn}$, where J_{exch} = exchange coupling and J_{magn} = magnetic coupling, and in the studied Cp_2NbH_3 the two constants are of opposite sign. An exhaustive study [17] has been also carried out for the tantalum and niobium trihydrides containing silylated cyclopentadienyl rings, namely Cp'_2MH_3 and Cp''_2MH_3 (M = Nb, Ta). As in Cp_2NbH_3, but unlike the corresponding tantalum derivatives, the niobium trihydrides show exchange coupling in their high-field ^1H NMR spectra due to a hydride tunneling phenomenon. The magnitudes of the exchange coupling are larger in the cases of Cp'_2NbH_3 and Cp''_2NbH_3 than in the case of Cp_2NbH_3, and this is a result of the decrease in electron density upon increasing the number of $SiMe_3$ substituents on the Cp ring. The tantalum trihydride derivatives show an AB_2 pattern at high field for the hydride ligands with coupling constants of ca. 10 Hz that are not dependent upon the temperature. In contrast, the niobium complexes Cp'_2NbH_3 and Cp''_2NbH_3 show an AB_2 pattern at r.t. for the hydrides, but in this case they are characterized by large coupling constants (36.5 and 70 Hz, respectively) that vary with temperature but not with the magnetic field. Further lowering of the temperature did not lead to the reappearance of this coupling. The longitudinal relaxation time, T_1, for the trihydrides Cp'_2NbH_3 and Cp''_2NbH_3 were measured. It was found that all hydrides show the same minimum of 40 and 55 ms, respectively, at 205 K (the value should be corrected to 100 ms when the influence of the Nb–H dipole–dipole relaxation is accounted for). In spite of the large number of studies performed on hydrogen exchange coupling in several polyhydride complexes, the exact physical processes accounting for the observation of the phenomenon still remain open to discussion. Zilm and colleagues have proposed a vibrational model to explain this coupling [15] whereas other authors have proposed that rotational tunneling of dihydrogen in a thermally accessible dihydrogen state could account for it [18]. Indeed, ab initio calculations show that niobium trihydrides possess a hydrido dihydrogen state that is almost degenerate in energy, whereas such a state is much higher in energy in the case of tantalum trihydrides [19]. Furthermore, a number of ab initio electronic energy calculations using a one-dimensional tunneling model have recently been carried out on metallocenes $[Cp_2MH_3]^{n+}$[M = Mo, W, ($n = 1$) and M = Nb, Ta ($n = 0$)], establishing that the stability of the η^2-H_2 structure relative to the minimum energy trihydride is the main parameter governing the magnitude of the exchange coupling [20]. In the search for a chemical discrimination between a purely vibrational mechanism and one implying rotational tunneling of dihydrogen, the addition of a Lewis acidic coinage cation to the niobocene trihydrides containing silylated cyclopentadienyl rings was extensively considered. Such additions were expected to inhibit the vibrational mode proposed to be at the origin of exchange coupling in Zilm's model. In particular, the addition of copper, silver or gold cations to the trihydride niobocene complexes Cp_2NbH_3, Cp'_2NbH_3 or Cp''_2NbH_3, was considered [17,21]. In fact, these complexes react with $[Cu(MeCN)_4]PF_6$, $AgBF_4$, and '$Au(THT)PF_6$', in a 2:1 ratio to yield the adducts $[\{Nb(C_5H_3RR')_2H_3\}M]^+$ (M = Cu, R = R′ = H; R = H, R′ = $SiMe_3$; R = R′ = $SiMe_3$; M = Ag, R = H, R′ = $SiMe_3$; R = R′ = $SiMe_3$; M = Au, R = R′ = H; R = H, R′ = $SiMe_3$; R = R′ = $SiMe_3$) (Scheme 1).

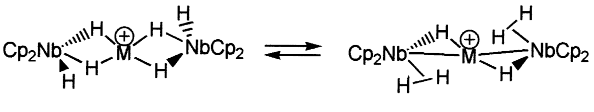
The addition of a Lewis acid cation results in the observation of an AB_2 pattern for the hydrides at r.t., which is split into an ABC pattern at low temperature. This



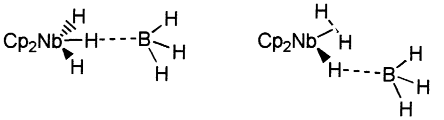
Scheme 1. Adapted from Ref. [17].

fact is in agreement with a fluxional behavior of the cation that binds to two hydrides of each niobium center. This structural situation has been confirmed by means of an X-ray crystal structure determination for the gold adduct with the $C_5H_3(SiMe_3)_2$ ring. The activation energies of these fluxional processes are close to 42–45 kJ mol^{-1} in the case of Cu adducts, 37 kJ mol^{-1} in the case of Ag adducts, and 40 kJ mol^{-1} in the case of Au adducts. The magnitude of the exchange coupling is reduced upon addition of the copper cation, it is of the same order of magnitude after addition of a silver cation, and is greatly increased by addition of a gold cation (Scheme 2).

A model has been proposed to explain these variations which involves two isomeric states that are close in energy, one involving two bridging and one terminal hydride ions on niobium and one involving one bridging hydride and a dihydrogen molecule. The difference in the magnitude of the exchange coupling between the coinage elements has been explained as follows. The fact that the presence of copper inhibits exchange coupling could arise from the stabilization of the dihydrido-bridged form, which could result from the good Lewis acid character of the copper cation. Furthermore, a coordination number of 2, although not impossible, is unlikely for copper. When the copper is substituted by silver or gold, the presence of a more extended electronic cloud will render the coinage cations less acidic and therefore less strongly bound to the hydrides. This could explain both the higher classical fluxionality and the increase in exchange coupling for silver compared to copper. However, the very significant increase in exchange coupling, but decrease in fluxionality, of the gold adducts compared to the silver ones looks anomalous. It has been proposed that this probably results from a stabilization of the dihydrogen form, perhaps through electron donation from the niobium(III) center to the gold cation. This type of interaction was previously observed in a related niobium/gold raft cluster [22]. Furthermore, an excellent model of the isomeric state with a bridging hydride and a dihydrogen molecule with copper, in which H_2 was substituted by CO, has been isolated and characterized by an X-ray crystal structure determination [23]. In order to theoretically study the stabilization of the η^2-H_2-containing state as a thermally accessible state in the trihydride niobocenes, different studies have been carried out more recently. For the first time,



Scheme 2. Adapted from Ref. [17].

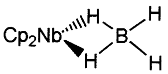


Scheme 3. Adapted from Ref. [24].

ab initio DFT calculations have been presented [24] that indicate that the formation of an adduct between a trihydride complex, Cp_2NbH_3, and a Lewis acid, BH_3, converts the dihydrogen structure into a stable complex. In fact, very interestingly, the interaction of BH_3 with a lateral hydride leads to the formation of a dihydrogen complex. This structure is only 3.3 kcal mol^{-1} above the trihydride structure in energy (Scheme 3).

The formation of this stable η^2-H_2 complex can be attributed to the diminution of the electronic density at the niobium metal caused by the presence of the Lewis acid attached to one of its hydride ligands. The authors have also considered the elimination of molecular hydrogen from the original trihydride complex. The final product of this process confirms the formation of the $Cp_2Nb(\eta^2$-$BH_4)$ (Scheme 4).

Following the study on the effect of a Lewis acid on the quantum exchange coupling in niobocene trihydrides, by means of the density functional methodology (DFT), this effect has also been calculated for the different adducts and transition states that appear in the $Cp_2NbH_3{\cdot}AlH_3$ system [25]. A Lewis acid of the AlH_3-type may increase the exchange coupling through formation of an adduct where the Lewis acid is only bonded to the outer hydride. In this structure, which is not the absolute minimum but is close enough in energy to be significantly populated at the experimental range of temperatures, the two 'free' hydrides came closer to each other so that an incipient dihydrogen ligand that favors the exchange tends to be formed. Finally, the incoherent contribution to the tunneling exchange of hydrogen pairs in the complex Cp''_2NbH_3 has been investigated [26] by ^1H NMR line-shape analysis and two-dimensional ^1H NMR exchange spectroscopy. The experimental data were analyzed by fitting them with simulated one- and two-dimensional spectra, taking into account the coherent and incoherent tunneling contributions and nuclear cross relaxation. The dissipative exchange process shows an Arrhenius-like temperature dependence with an activation energy $Ea = 69(2)$ kJ mol^{-1} over the temperature range 246–341 K.



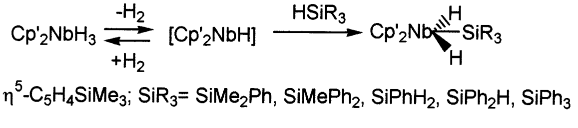
Scheme 4. Adapted from Ref. [24].

3. σ-Bond activation by niobocene and tantalocene hydrides

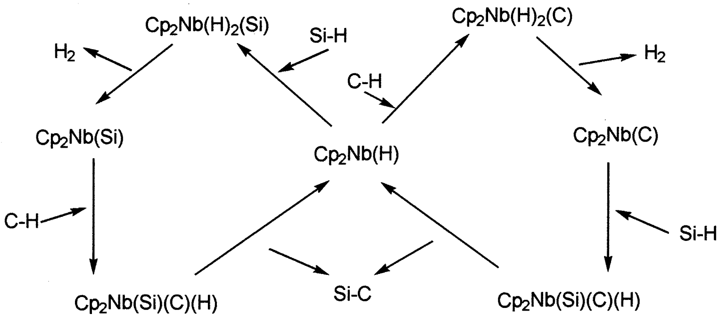
Activation of σ-bonds, principally C–H bonds, by transition metal complexes is currently an area of intense research activity, and several important advances in this area have recently been reported [27]. Although late metal complexes are usually applied to these reactions, Cp_2MH_3 complexes ($Cp = C_5H_5$; M = Nb, Ta) catalyze [7a,28] H/D exchange between H_2 and C_6D_6, as well as the exchange between PhH and $AlEt_3$. In a similar way [9], these trihydride derivatives react with hydrosilanes, $PhMe_2SiH$, to give the appropriate silyl complexes $Cp_2M(H)_2(SiMe_2Ph)$. This method was extended [29] to niobocene trihydride complexes bearing electron-withdrawing substituents, $SiMe_3$, in the cyclopentadienyl rings (Scheme 5), and gave rise to the corresponding niobocene silyl dihydride species.

The initial step, presumably, is the formation of the $16e^-$ coordinatively unsaturated Cp'_2NbH by thermolytic loss of H_2 (see Scheme 5). This process is then followed by oxidative addition of the organosilicon hydride, so that a closed-shell $18e^-$ configuration in the silyl dihydride derivative is achieved. A similar intermediate was proposed by Berry et al. [30] for the thermolysis ($> 100°C$), or photolysis (350 nm) of $Cp_2Ta(L)(H)$ (L = CO, PMe_3, $CH_2{=}CH_2$, H_2) in the presence of hydrosilanes, to afford the corresponding tantalum silyl dihydrides $Cp_2Ta(H)_2(SiR_3)$ ($SiR_3{=}SiH_3$, $SiMe_2H$, $SiMe_3$, $SiMe_2Cl$, $Si(OMe)_3$). Cp_2NbH_3 has been found [9] to be an excellent catalyst for the redistribution of groups on silicon. Heating a solution of $HSiMe_2OSiMe_3$ and Cp_2NbH_3 in benzene gave rise to a small amount of conversion of the pentamethylsiloxane into higher polysiloxanes. The reaction presumably involves oxidative addition of Si–H, Si–C, and Si–O bonds onto a low-valent metal species. In a stoichiometric reaction, the compounds isolated were the starting materials and $Cp_2Nb(H)_2(SiMe_2OSiMe_3)$. It was expected that the complex Cp_2NbH_3 could catalyze the formation of phenylsilanes in a productive activation process according to Scheme 6 [9], due to the fact that it catalyzes H/D exchange between H_2 and C_6D_6 [7a].

However, heating a 1:10 mixture of Cp_2NbH_3 and $PhMe_2SiH$ in C_6D_6 to 60°C for 16 h gave a quantitative conversion of Cp_2NbH_3 into $Cp_2Nb(H)_2(SiPhMe_2)$ and the excess $PhMe_2SiH$ was found to be ca. 2% monodeuterated. When Et_3SiH was used, 20% of d^1 Et_3SiH was recovered. To explain why phenylsilanes are not formed even though both the C–D and Si–H bonds are activated by the niobium complex, the stereochemistry of the oxidative addition on the monohydride niobocene intermediate must be considered. This oxidative addition can give rise to two isomers, i.e. symmetrical and asymmetrical (Scheme 7).



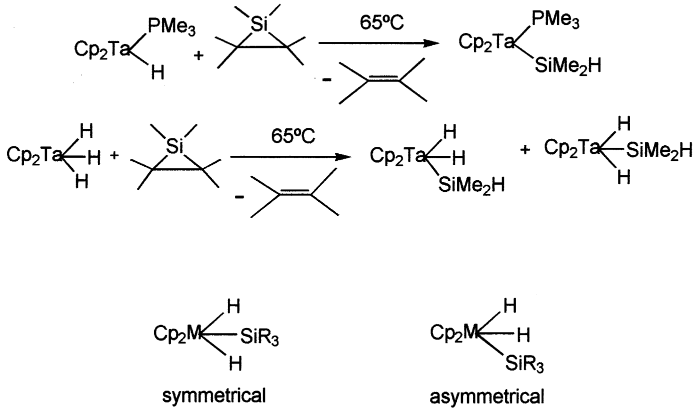
Scheme 5. Adapted from Ref. [29].



Scheme 6. Adapted from Ref. [9].

The silyl derivatives described above were widely characterized by NMR and X-ray diffraction studies. These techniques showed the presence of only the symmetrical isomer with the silyl group in the central position replacing the central hydrogen. As the asymmetrical isomer was not formed, productive activation was not observed. The asymmetrical complexes could eliminate the *cis* hydrides as H_2 and form intermediates that could add new Si–H or C–H bonds to give a productive activation process (Scheme 6). Although stable $Cp_2Nb(H)_2(Ar)$ complexes have not been isolated, it is reasonable to assume that the Ar group will also occupy the central position in this process. This would give the symmetrical isomer and non-productive activation would also take place.

However, a mixture of symmetrical and asymmetrical isomers was obtained [30] in the photochemical reactions between $Cp_2Ta(H)(L)$ and hydrosilanes. The minor asymmetrical isomer could not be isolated from the mixture and isomerizes, by means of an intramolecular exchange, to the thermodynamically stable symmetrical isomer. Alternative routes have been described [31] to obtain asymmetrical dihydride silyl complexes. The transfer of a silylene to tantalum hydride complexes proceeds by the insertion of this silylene into the Ta–H bond (Eqs. (1 and 2)).

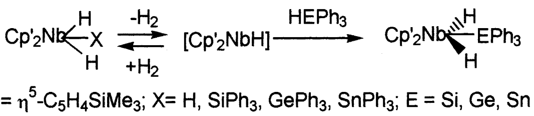


(1)

(2)

Scheme 7.

In the reaction shown in Eq. (2), a 9:1 mixture of symmetrical and asymmetrical complexes was obtained. In order to complete the series of dihydride niobocene derivatives containing Group 14 fragments, analogous d^0 niobocene germyl and stannyl complexes, $Cp'_2Nb(H)_2(ER_3)$ ($ER_3 = SnPh_3$, $GePh_3$, $GePh_2H$, $GeEt_3$, $Ge(C_6H_{13})_3$, $Ge[(CH_2)_2CH(CH_3)_2]_3$, $Ge(C_6H_{13})_2Cl$, $Ge[(CH_2)_2CH(CH_3)_2]_2Cl$, $Ge(C_6H_{13})_2H$, $Ge[(CH_2)_2CH(CH_3)_2]_2H$) have been prepared [32] by the reaction between Cp'_2NbH_3 and several organogermanium hydrides, $HGeR_3$, or $HSnPh_3$, in toluene at 65°C. This is the first time that d^0 early metal germyl complexes have been prepared by oxidative addition of organogermanium hydrides to coordinatively unsaturated hydride substrates. In a similar way to the silyl niobocene complexes described above, these germyl or stannyl derivatives show a symmetrical disposition with respect to the niobium center. Although the germyl niobocene complexes are the first described, precedents of the analogous stannyl complex were reported by Lappert [33] and Green [34]. Thus, the compound $Cp_2Ta(H)_2(SnMe_3)$ was prepared by the reaction of the trihydride with $SnMe_3(NMe_2)$. In an alternative approach, the addition of BuLi to a toluene solution of Cp_2NbH_3 gave rise to a solid described as $[\{Cp_2NbH_2Li\}_x]$, which can be isolated as a stable [Li(12-crown-4)][$NbCp_2H_2$] salt. Addition of one equivalent of $SnMe_3Cl$ to this niobium complex led to the isolation of the complex $Cp_2Nb(H)_2(SnMe_3)$. The possibility that the two hydrogens would be present as a dihydrogen (η^2-H_2) ligand in this last complex was ruled out by the preparation of the deuterium-substituted complex $Cp_2Nb(H)(D)(SnMe_3)$ by the reaction of Cp_2NbH_3 with $SnMe_3D$. The ^1H NMR spectrum of the complex shows an unresolved H–D coupling in the broad hydride signal, with $J(H\text{–}D) < 10$ Hz. This may be compared with the typical values of molecular hydrogen complexes ($22 < J(H\text{–}D) < 36$ Hz). The hydride T_1 relaxation time reaches a minimum of 116 ms at 183 K, indicative of a classical dihydride structure. This classical behavior is in contrast with the reactivity of this compound. In fact, the smooth reaction of $Cp_2Nb(H)_2(SnMe_3)$ with two-electron donor ligands, PMe_3 and styrene, occurred and resulted in the addition of the ligand and displacement of H_2. The elimination of H_2 would presumably require initial interchange of position of one hydrogen atom with the $SnMe_3$ ligand, possibly via an η^2-H_2 or η^2-$HSnMe_3$ intermediate. In the silyl dihydride derivatives that have been described, ^{29}Si NMR data can be used to detect the presence of a H···Si interaction. Corriu and co-workers [35] showed that the $^1J(Si\text{–}H)$ value for the agostic-like H···Si interaction is near to 65 Hz, thus appearing between that characteristic of classical silyl hydrides (≈ 6 Hz) and that of free silanes (≈ 200 Hz). The ^{29}Si NMR spectrum of $Cp'_2Nb(H)_2(SiPh_2H)$ [29] shows a doublet at $\delta = 23.8$ for the silyl group with $^1J(Si\text{–}H) = 17$ Hz. This coupling disappeared when the hydrogen of the silyl group was irradiated. In the ^1H NMR spectrum, the coupling is also observed for the resonance of this hydrogen atom and, in addition, the line width of the signals for the two hydride ligands (6 Hz) is characteristic of a classical silyl hydride. These spectroscopic data establish the classical nature of these silyl hydrides. However, in the solid state the molecular structure cannot exclude any interaction between the hydrides and the silicon atom on the basis of van der Waals radii, in a hypervalence mode for the silicon atom [36].



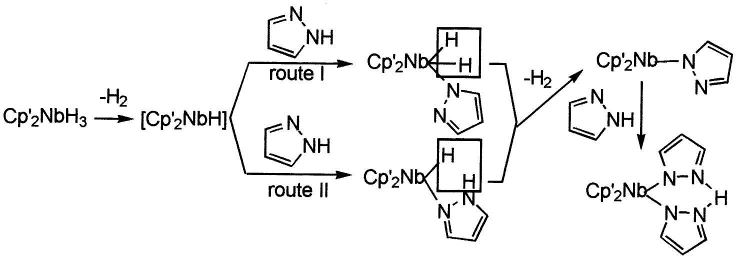
Scheme 8. Adapted from Ref. [29].

The reactivity of hydride-, silyl-, germyl- or stannyl-containing niobocene complexes towards the hydrides $HEPh_3$ (E = Si, Ge, Sn) in σ-bond metathesis reactions of d^0 Nb–E bonds with H–E′ σ bonds have been studied [32] (Scheme 8). The reactions were monitored by ^1H NMR spectroscopy. From these studies the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were obtained. These parameters allow the estimation of the bond dissociation enthalpies, which were found to be comparable to Nb–H, Nb–Si, Nb–Ge and Nb–Sn bonds, with values near to 50 kcal mol^{-1}.

However, the experimental results indicate the following reactivity trend: $Nb–H \approx Nb–Si > Nb–Ge \gg Nb–Sn$ for the σ-bond metathesis processes. In fact, Cp'_2NbH_3 reacts with $HEPh_3$ (E = Si, Ge, Sn), $Cp'_2Nb(H)_2(SiPh_3)$ reacts with H_2, $HGePh_3$ or $HSnPh_3$, $Cp'_2Nb(H)_2(GePh_3)$ reacts with $HSnPh_3$, but $Cp'_2Nb(H)_2(SnPh_3)$ does not react with either H_2, $HSiPh_3$ or $HGePh_3$. The results can be rationalized in terms of differences in reactant and product bond strengths. The energy required to break the Nb–H, Nb–Si or Nb–Ge bonds is compensated by formation of relatively strong H–H, H–Si and H–Ge bonds in the HX molecule eliminated in the first step (see Scheme 8). In contrast, the formation of the weaker H–Sn bond does not compensate the energy required to break the strong Nb–Sn bond. A similar explanation has been postulated by Tilley et al. [37] to rationalize the reactivity trends of analogous d^0 zirconocene complexes in bond metathesis reactions that parallel those described above in the niobium system.

Recently, a similar dihydride niobocene containing a $PbMe_3$ moiety, namely $Cp_2NbH_2(PbMe_3)$, was described [38a] to complete the family of niobocene dihydride-containing Group 14 fragments. This compound was prepared by reacting Cp_2NbH_3 with $ClPbMe_3$ in the presence of amine to eliminate HCl.

A number of other main group element–hydrogen bonds can be activated by the trihydride niobocene complex. Thermolysis of Cp'_2NbH_3 in the presence of pyrazole gives rise to a pyrazolyl–pyrazole niobocene, $Cp'_2Nb(pzH)(pz)$ [39a] (Scheme 9).



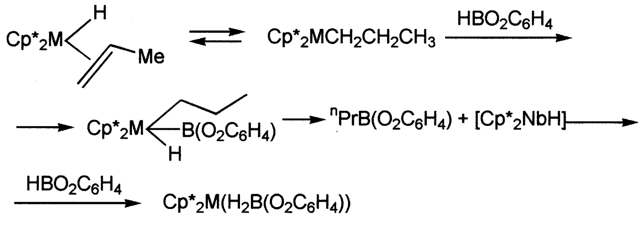
Scheme 9. Adapted from Ref. [39a].

Two mechanisms can be envisaged for the formation of this complex. In the first possibility (Scheme 9, route I), N–H bond activation leads to an asymmetrical dihydride intermediate, which loses H_2 and coordinates the second molecule of pyrazole. A second possibility (Scheme 9, route II) involves pyrazole coordination by a pyridine nitrogen as the first step. Subsequently, the monohydride–pyrazole complex evolves with protonation, probably in an intramolecular mode with the loss of H_2. Finally, coordination of the second pyrazole substituent takes place. Activation of P–H bonds was also observed [39b] in the reactions of Cp_2MH_3 (M = Nb, Ta) with an excess of primary phosphines. These reactions yield the diphosphonato complexes $Cp_2Nb(H)\{(PPh)_2\}$, $Cp'_2Nb(H)\{(PPh)_2\}$, and $Cp_2Ta(H)\{(PPh)_2\}$. The insertion of Group 15 halogenides into the M–H bond is an alternative route to bond activation for the synthesis of main-group element-substituted niobocene and tantalocene hydrido complexes. Phosphorus or arsenic monohalogenides $ClPPh_2$ [38b,c], or $BrAsR_2$ (R = Me, Et) [38d], insert easily into the M–H bond of Cp_2MH_3 to afford the ionic complexes $[Cp_2MH_2(HER_2)]X$ (M = Nb, Ta, E = P, R = Ph, X = Cl; M = Nb, E = As, R = Me, Et, X = Br). Deprotonation of these complexes with a base, i.e. NEt_3 or aqueous NaOH, gives rise to the hydride phosphino-, arsenido- or phosphido derivatives $Cp_2NbH(PPh_3)$, $Cp_2NbH_2(AsR_2)$ and $Cp_2TaH_2(PPh_2)$.

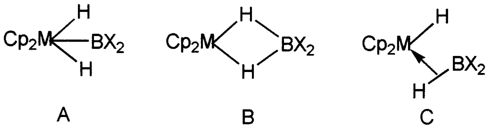
In recent years, niobocene complexes containing metal–boron bonds, $Cp_2Nb(H_2BR_2)$ ($R_2 = O_2C_6H_4$, C_8H_{14}), were prepared [40] by the reaction between Cp_2NbH_3 and hydroboranes. Analogous compounds, $Cp^*_2M(H_2B(O_2C_6H_4))$, were obtained from the reaction between $Cp^*_2M(CH_2{=}CH(R))(H)$ ($Cp^* = C_5Me_5$, M = Nb, Ta) and two equivalents of catecholborane. In the last case, experimental results are consistent with a mechanism involving an unsaturated alkyl intermediate (Scheme 10) that activates the H–B bond.

As an alternative, analogous tantalocene complexes $Cp_2Ta(H)_2(B(O_2C_6H_4))$ in the form of their symmetrical and asymmetrical isomers can be obtained [42] by the reaction between $[\{Cp_2TaH_2Li\}_x]$ and $ClBO_2C_6H_4$. For these $Cp_2MH_2BX_2$ (Cp = C_5H_5 or C_5Me_5) complexes, three limiting forms can be used to describe the H_2BX_2 coordination. These include d^0 boryl (A), d^2 borohydride (B), and d^2 agostic borane (C) structures (Scheme 11).

While tantalum complexes are clearly characterized as boryl complexes of type A, the niobium ones show a pronounced Nb(III) character. For catechol-containing niobocene derivatives, equilibria between situations A and B were proposed on the



Scheme 10. Adapted from Ref. [41].



Scheme 11.

basis of spectroscopic data and isotopic perturbations of their NMR spectra. Spectroscopic data support some B–H interaction for *exo*-$Cp_2TaH_2(BO_2C_6H_4)$, although the sum of the angles about boron, from the molecular structure, is consistent with an sp^2 hydrization at the boron atom and suggests that this compound is a tantalum(V) boryl dihydride rather than an agostic borane of tantalum(III).

4. The chemistry of d^2 hydride niobocene and tantalocene derivatives

In this chapter the most extensive family of hydride metallocene complexes of niobium and tantalum will be considered, and this family corresponds to the 18-electron d^2 Cp_2MHL ($M = Nb$, Ta, $L = \pi$-acid ligand). Complexes have been described with different classes of π-acid ligands obtained by several types of preparation processes. In the following discussion, the hydride–olefin metallocenes have been treated in a different section than the rest of complexes due to their special significance in catalysis.

4.1. Preparations

Table 1 includes references to various preparations of these complexes with different types of cyclopentadienyl rings.

The thermal treatment of Cp_2MH_3 species in the presence of L constitutes the most important process for the preparation of a huge family of Cp_2MHL complexes ($L = \pi$-acid ligand). In most of the cases, the processes are not facile because harsh conditions (reflux in toluene during several days) for the elimination of H_2 and the subsequent coordination of the π-acid ligand are necessary. Moreover, the substitution is frequently incomplete so that the new Cp_2MHL derivative contains impurities. Extensive families of complexes with different classes of both cyclopentadienyl rings and π-acid ligands, especially carbon monoxide or phosphine, have been thoroughly described and these are collected in Table 1. However, the Cp'_2MH_3 ($M = Nb$, Ta, $Cp' = \eta^5$-$C_5H_4SiMe_3$) complexes react easily [48,49,56] with π-acid ligands, using THF as solvent, to quantitatively give several hydride complexes, Cp'_2MHL. Thus, Cp'_2NbH_3 reacts under mild conditions in THF with phosphites to give new hydride niobocene complexes $Cp'_2NbH(P(OR)_3)$. Similarly, the easy preparation in high yields (95%) [56] of hydride–isocyanide complexes has recently been reported: $Cp'_2NbH(CNR)$ ($R = {}^tBu$, Cy, Xylyl) by thermal treatment in THF of Cp'_2NbH_3 in the presence of the corresponding isocyanide. No subse-

Table 1
d^2 Hydride complexes of niobium and tantalum, Cp_2MHL, M = Nb, Ta, L = π-acid ligand

$Cp_2MH_3 + L \rightarrow Cp_2M(H)L$		
(a) M = Nb	Cp = C_5H_5	L = CO, PMe_3, PEt_3 [43], Ph_2H [45], N_2CPh_2 [46], PMe_2Ph [47], $^nPrCC^nPr$, $MeCC^nPr$, MeCCMe, $MeCC^iPr$ [53], EtCCEt, PhCCPh, TMSCCTMS [50,54], CF_3CCCF_3 [55]
	Cp = $C_5H_4SiMe_3$	L = CO, $P(OMe)_3$, PhCCPh [48], $P(OEt)_3$, $P(OPh)_3$ [49], CN^tBu, CNCy, CNXylyl [56]
	Cp = $C_5H_4{}^tBu$	L = CO [57]
	Cp = C_5Me_5	L = CO [60], MeCCMe [61]
	Cp = $C_5H_3(SiMe_3)_2$	L = CO [6]
	CpCp′ = $(C_5H_5)(C_5Me_5)$	L = CO, MeCCMe [61]
(b) M = Ta	Cp = C_5H_5	L = CO, PEt_3, MeCCMe, PhCCPh, TMSCCTMS [43], PMe_2Ph, $P(OMe)_3$ [44], N_2CPh_2 [46], $^iPrCC^iPr$ [51], $^tBuCC^tBu$ [52]
	Cp = $C_5H_4SiMe_3$	L = CO [57b]
	Cp = $C_5H_4{}^tBu$	L = CO [57]
	Cp = C_5Me_5	L = MeCCMe [61]
	Cp = $C_5H_4{}^iPr$	L = CO [58]
	Cp = C_5H_4R R = CMe_2Ph, CHMePh	L = CO [57b,59]
	CpCp′ = $(C_5Me_5)(C_5H_3(SiMe_3)_2)$	L = CO, CNXylyl [62]

quent insertion process was observed even when the process was carried out with an excess of ligand in refluxing THF for a long time. This behavior contrasts with that found for hydride Group 4 metallocenes, where the insertion process to give iminoacyl derivatives is especially favoured [63]. In these processes, the initial step would be the formation of the coordinatively unsaturated 16-electron species 'Cp_2MH' by thermolytic loss of H_2 followed by the coordination of the π-acid ligand. The mechanism for the formation could be explained in terms of a model, which implies a consecutive reaction with a reversible step and a first-order rate dependence with respect to Cp_2MH_3 [64]. On the other hand, an alternative preparation of Cp_2MHL complexes has been described [65] involving the reaction of Cp_2MCl_2 with $NaBH_4$ followed by the addition of triethylamine in the presence of the appropriate π-acid ligand. Likewise, the reaction of Cp_2MCl_2 with $LiAlH_4$ in the presence of a phosphine (PMe_2Ph, PMe_3) allows the synthesis of the same class of complexes Cp_2MHL [47,66].

Alkyne-hydride derivatives constitute a special family of this type of complex (see Table 1). However, few alkyne–hydride complexes of niobium and tantalum have been isolated. Most of those that have, have been prepared by the reaction of Cp_2MH_3 complexes with the appropriate alkyne ligand.

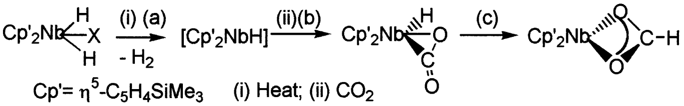
4.2. Reactivity of the Cp_2MHL and related species in insertion processes

In this section the reactivity of the hydride niobocene and tantalocene species, the d^2 Cp_2MHL complexes, will be discussed. In fact, many examples have been described of the insertion of unsaturated molecules into the M–H bond in hydride metallocenes of niobium and tantalum. In order to rationalize the discussion, the reactions with heterocumulene molecules will be considered first, and afterwards a specific group of insertion processes with alkynes will also be described.

4.2.1. Insertion processes with heterocumulene molecules

Insertion reactions of heterocumulenes, like that carbon disulfide, isocyanate or isothiocyanate, are especially interesting because they allow the modelling of the insertion reactions of carbon dioxide, a process that constitutes an attractive goal in the field of organometallic chemistry. The reaction of Cp_2MHL ($Cp = C_5H_5$, M = Nb, Ta, L = CO [67], $Cp = Cp' = C_5H_4SiMe_3$, M = Nb, L = CO, $P(OR)_3$ [49]) with CS_2 proceeds with the expected insertion of the heterocumulene into the M–H bond to give a dithioformate ligand, S(S)CH. The nature of the products for the Cp'_2NbHL is dependent on the nature of L. When L = CO, the new ligand exhibits an η^1-dithioformate coordination, whereas when L = $P(OR)_3$ an η^2-dithioformate species is present in the reaction product. In the latter case, an initial η^1-dithioformate complex is probably formed, with loss of phosphite, to give the final η^2-dithioformate ligand, which is, however, unusual in this type of insertion process. When the heterocumulene is isocyanate (RNCO) or isothiocyanate (RNCS) the insertion reaction into the M–H bond gives the new formamido- or thioformamido-containing $Cp_2M(\eta^1\text{-}XC(H)NR)(L)$ complexes ($Cp = C_5H_5$, M = Nb, Ta, L = CO, $PMePh_2$ [67,68], $Cp = Cp' = C_5H_4SiMe_3$, M = Nb, L = CO, CNR [69]). The subsequent protonation of $Cp'_2Nb(\eta^1\text{-}XC(H)NR)(L)$ complexes using CF_3COOH yields the trifluoroacetato complexes $Cp'_2Nb(\eta^4\text{-}OOCCF_3)(L)$ and the imine derivatives HOC(H)=NR and HSC(H)=NR. The interaction of a trihydride niobocene, Cp'_2NbH_3, with carbon dioxide was investigated because metalloformates M–OC(O)H derived from carbon dioxide insertion into M–H bonds are known to be involved in the catalytic hydrogenation of these compounds to formic acid and its derivatives [70]. The complex Cp'_2NbH_3 reacted with CO_2 to give the formate complex $Cp'_2Nb(OC(O)H,O,O')$ [71]. The isolation of this complex can be understood in terms of Scheme 12.

Step (a) corresponds to the elimination of H_2 and the formation of a very reactive 16-electron monohydride niobocene species, which has previously been proposed in several processes [64]. Coordination of CO_2 to this unsaturated species to give an

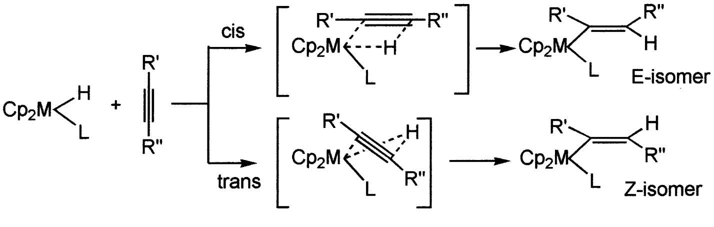


Scheme 12. Adapted from Ref. [71].

18-electron hydride–carbon dioxide intermediate is suggested in step (b). The final step (c) corresponds to the insertion of the coordinated CO_2 into the Nb–H bond to give the formate ligand. The formation of hydride–carbon dioxide tantalocene intermediate at −40°C, as well as the subsequent insertion to give formato tantalocene derivatives, has also been published [72]. Reactivity studies on the complex $Cp'_2Nb(OC(O)H,O,O')$ have been carried out. Reaction with CS_2 or the π-acid ligands CO and $2,6\text{-}Me_2C_6H_3NC$ gave rise to the transformation from a bidentate to a monodentate formate as a consequence of coordination of the incoming ligand, and the $Cp'_2Nb(OC(O)H,O)L$ complexes were isolated. However, with other L, such as phosphites $P(OR)_3$, the transformation has never been observed; this behavior suggests that the presence of a heterocumulene like CS_2, which is able to coordinate strongly to the niobium atom as a bidentate ligand or strong π acceptors, is necessary to break an Nb–O bond and to transform bidentate into monodentate formate.

4.2.2. Insertion processes with alkynes

The insertion of alkynes into transition metal–hydrogen bonds is a key elementary step in catalytic polymerization and hydrogenation processes [3b]. In the last few years, the stereochemistry and mechanism involved in the insertion process have received considerable attention [73]. Insertion results in the formation of alkenyl products and these show that *cis* and *trans*-insertion yield the (*E*)-alkenyl and (*Z*)-alkenyl products, respectively, and that the importance of the *cis*/*trans* stereochemistry depends on several factors, such as the nature of the metal center, ancillary ligands, and substituents on the alkyne. Electron-rich, coordinatively saturated, metallocene–hydride complexes of early transition metals react readily with activated alkynes bearing electron-withdrawing groups to give alkenyl complexes. Thus, in earlier work the behavior of niobocene–hydrides, especially $Cp_2NbH(CO)$, was extensively studied [73i,74] and most of the processes of hydride metallocenes with disubstituted activated alkynes occur by stereospecific *trans*-insertion reactions that give rise to kinetic products of (*Z*)-configuration [75], see Scheme 13. However, the hydride–isocyanide complexes $Cp'_2NbH(CNR)$ ($R = $ xylyl = 2,6-dimethylphenyl, Cy, ^{t}Bu, $Cp' = \eta^5\text{-}C_5H_4SiMe_3$) react with several activated alkynes to afford the corresponding alkenyl–isocyanide complexes $Cp'_2Nb(CNR)(C(R')\text{=}CH(R''))$ though a stereospecific *cis*-insertion (see Scheme 13) resulting in the formation of (*E*)-alkenyl products [76].



Scheme 13. Adapted from Ref. [76].

As a consequence of these results, it has been established that in the presence of bulky ancillary ligands, such as some isocyanides, a primary *cis* stereospecific insertion under kinetic control affords the (*E*)-isomer, probably via the four-centered transition state shown in Scheme 13, which is favoured by steric arguments. In the same reaction for $Cp'_2NbH(CO)$ with the activated alkynes, under kinetic control, a mixture of (*E*)- and (*Z*)-alkenyl niobocene complexes, $Cp'_2Nb(CO)$-$(C(R')=CH(R''))$, was obtained. It has been proposed that a primary *trans* stereospecific insertion would occur via a four-centered transition state to give the kinetic (*Z*)-isomer and a subsequent isomerization would give the (*E*)-isomer, resulting in the mixture of (*E*)- and (*Z*)-isomers. The results obtained in the reaction of the trihydride metallocenes, namely Cp_2TaH_3 and Cp_2NbH_3, with activated alkynes are particularly interesting [50,76]. In fact, these complexes react with activated alkynes, such as $RO_2CC{\equiv}CCHR'$, to afford new hydride–olefin complexes, $Cp_2Ta(H)$(*trans*-$RO_2CCH{=}CHCO_2R'$) and $Cp_2Nb(H)$(*trans*-$RO_2CCH{=}CHCO_2R'$). This behavior is surprising because reactions of these trihydride metallocenes with alkynes are well known and generally give rise to alkyne–hydride metallocenes [53,55,77]. In order to explain the formation of these complexes, a stereospecific *trans*-insertion to give a dihydride alkenyl intermediate is suggested in the first step, followed by an intermolecular rearrangement that leads to the final hydride–olefin complexes.

4.3. Reactivity of the Cp_2MHL complexes in protonation processes: synthesis of dihydrogen complexes

The d^2 Cp_2MHL complexes behave as Lewis bases and therefore they can be protonated at r.t. by acids to give the corresponding cationic complexes, which have been isolated as the *trans*-$[Cp_2MH_2L]^+$ cationic dihydride species [44,78]. Thus, the complexes Cp'_2NbHL ($Cp' = \eta^5$-$C_5H_4SiMe_3$) were protonated with $[PhNH_3]PF_6$ in THF, allowing the isolation of the corresponding transoid cationic niobocene dihydrides *trans*-$[Cp'_2Nb(H)_2L]$ PF_6. In the same way, *trans*-$[Cp_2Ta(H)_2(CO)]PF_6$ was obtained by protonation of $Cp_2TaH(CO)$ ($Cp = \eta^5$-C_5H_5) with aqueous HCl at r.t. However, different results have been found in recent years when the protonation processes were carried out at low temperatures, since dihydrogen-containing metallocene species were stabilized. Protonation of a neutral hydride complex to give a cationic dihydrogen complex was first reported by Crabtree et al. [79]. Subsequently, numerous examples have been described [5]. A number of different families of dihydrogen-containing niobocene and tantalocene complexes have been described following this method. The tantalocene complex $[Cp_2Ta(\eta^2$-$H_2)(CO)]^+$ was prepared [80] by protonation of $Cp_2TaH(CO)$ ($Cp = C_5H_5$, $C_5H_4^tBu$) at low temperature. The relaxation time, T_1, of the hydrides shows a minimum of 9 ms (for C_5H_5) and 12 ms (for $C_5H_4^tBu$) at 178 K, which corresponds to dihydrogen complexes. Halpern's approximate equation [81] leads to a H–H distance of 0.84 ± 0.05 Å (for C_5H_5) and 0.89 ± 0.05 Å (for $C_5H_4^tBu$). It is interesting to note the variation of the relaxation time of the hydride signals of both isomers when C_5H_5 is replaced by $C_5H_4^tBu$. This is due to the difference in the electronic properties of the Cp ligands:

the more electron releasing ligand $C_5H_4'^tBu$ induces a lengthening of the H–H bands. In the deuterated complex $[Cp_2Ta(\eta^2\text{-HD})(CO)]^+$ the J_{HD} value is 26.5 Hz, which is in agreement with an unstretched dihydrogen structure. When CF_3CO_2H was added to an acetone-d^6 solution of $Cp_2'NbHL$ ($Cp' = \eta^5\text{-}C_5H_4SiMe_3$, $L = P(OEt)_3$, PMe_2Ph) at −90°C in an NMR tube, dihydrogen-containing niobocene complexes $[Cp_2Nb(\eta^2\text{-H})L]^+$ were stabilized [78c]. When the temperature was increased the complex with $L = P(OEt)_3$ transformed into its transoid isomer through an irreversible process. Increasing the temperature did not produce the transoid form of the complex with $L = PMe_2Ph$, but its qualitative transformation at 20°C into $[Cp_2'Nb(CF_3CO_2)(PMe_2Ph)]$. The analogous $[Cp_2'Nb(CF_3CO_2)(CO)]$ is the only niobium compound observed at all temperatures when the complex $Cp_2'NbH(CO)$ is reacted under similar conditions with CF_3CO_2H, probably because the large π-accepting character of the CO ligand prevents stabilization. The T_1 minima were found to be 24 ms at 188 K and 19 ms at 196 K for the dihydrogen complexes with $L = P(OEt)_3$ and $L = PMe_2Ph$, respectively. H–H distances of 0.97 Å, assuming rapid rotation of dihydrogen, and 1.22 Å, assuming a slow rotation, and 1.17 Å for the aforementioned complexes were also calculated. A value of $J_{HD} = 18.2$ Hz was also found in the deuterated complex $[Cp_2'Nb(\eta^2\text{-HD})P(OEt)_3]^+$, and this value is in good agreement with the distance calculated from T_1 data. One of the most interesting points of the hydrogen-containing tantalocene and niobocene complexes described [78c,80] lies in the fact that activation barriers for the rotation of H_2 are surprisingly high (ca. 10 kcal mol^{-1}), therefore providing an intermediate case between the normal dihydrogen complex and the polyhydride complexes. As a consequence of the high barrier, rotation of the dihydrogen molecule seems to be blocked from the NMR line scale [78c,82]. For these complexes a single resonance is obtained for the ^1H NMR spectra at high temperatures. When the temperature is lowered, decoalescence is not observed for the nonisotopically substituted H_2 isomer, but it is observed for the partially deuterated HD species. This has allowed estimation of the activation barriers for these complexes. This surprising result has been explained by the postulation of a large exchange coupling in the H_2 case. It is known [82] that for $J/\Delta\delta$ ratios higher than 10, the expected AB-type spectrum becomes a single line. Although it is expected that H–H and H–D have very similar barriers for the rotation, there is no direct experimental evidence that the H–H rotation is also being practically blocked. From a theoretical point of view, the rotational barrier for the H–H rotation has been calculated for the simplified model complexes $[Cl_2Ta(\eta^2\text{-}H_2)CO]^+$ and $[Cl_2Ta(\eta^2\text{-}H_2)(PH_3)]^+$ to be 9.7 and 11.3 kcal mol^{-1}, respectively [82]. It was necessary to obtain a new experimental example of a non-rotating coordinated H–D molecule in order to analyze its structure and the hydrogen exchange process. Such an example would provide theoretical evidence that in the corresponding H–H molecule this process is also classically blocked at the NMR time scale and allow the estimation of the order of magnitude of the exchange coupling. For these reasons new dihydrogen niobocene complexes were prepared [56]. In fact, low-temperature protonation of hydride isocyanide derivatives $Cp_2'Nb(H)(CNR)$ ($Cp' = \eta^5\text{-}C_5H_4SiMe_3$) with a slight excess of CF_3CO_2H led to the dihydrogen complexes $[Cp_2'Nb(\eta^2\text{-}H_2)(CNR)]^+$. The monodeuterated complexes have also been prepared and coupling constants J_{HD} of ca. 30 Hz verify the presence of a H–D bond and provide effective proof of the presence of an unstretched dihydrogen complex. H–H distances between 1.01 and 1.06 Å were found assuming slow H_2 spinning. The NMR spectra of these H–H complexes and their monodeuterated H–D isotopomers show a single high-field resonance at r.t. On lowering the temperature to 178 K, decoalescence of the signal was observed for the H–D complexes but not for the H–H ones. By combining DFT electronic structure calculations with a monodimensional rotation tunneling model, it has been shown that the absence of decoalescence of the H–H signal is due to the existence of a very large exchange coupling. Conversely, for the H–D isotopomers, the difference in zero point energy corresponding to two nonequivalent (H–D and D–H) positions leads to a slight asymmetry, which dramatically reduces the exchange coupling, allowing decoalescence to be observed. Therefore, the H–D classical rotation and the quantum exchange processes will not be practically observed for this complex, whereas only the classical case for the H–H species is quenched out on the NMR time scale.

4.4. The hydride–olefin niobocene and tantalocene complexes

Olefin–hydride metal systems, including those corresponding to Group 5 metals, are of great interest in a host of catalytic processes. After the preparation of the first olefin–hydride bis-(cyclopentadienyl) complex of Group 5 metals, $Cp_2Nb(H)(\eta^2\text{-}C_2H_4)$ ($Cp = \eta^5\text{-}C_5H_5$) by Tebbe and Parshall [7a], several olefin–hydride complexes of Nb and Ta were synthesized by employing two alternative processes, namely the reactions of Cp_2MCl_2 and Cp_2MH_3 ($M = Nb$, Ta) with various alkylmagnesium halides and olefins, respectively.

4.4.1. Preparations

The first niobocene and tantalocene olefin–hydride complexes have been prepared by the reaction of Cp_2MH_3 with the corresponding olefin. This process takes place through thermal elimination of H_2 followed by olefinic coordination on the Cp_2MH species Eq. (3).

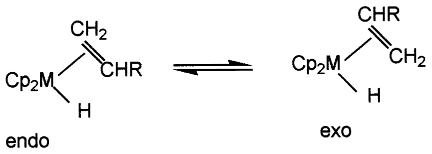
$$(C_5R_5)_2MH_3 \;+\; R'CH{=}CH_2 \longrightarrow (C_5R_5)_2M(H)(CH_2{=}CHR') \;+\; H_2 \qquad (3)$$

M = Nb, Ta. R = H; R' = H. [7a]

M = Nb. R = Me; R' = H, Ph, *p*-$Me_2NC_6H_4$, *p*-$MeOC_6H_4$, *p*-MeC_6H_4, *p*-$CF_3C_6H_4$. [83]
    $R_5 = H_4SiMe_3$; R' = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$. [64, 84]

M = Ta. R = H; R' = Me. [85]

In contrast to the complexes $(C_5R_5)Nb(H)(olefin)$ ($R_5 = H_5$; H_4SiMe_3), in which both *endo* and *exo* isomers are observed, when R = Me the product is obtained in a single isomeric form. Models indicate that the *endo* isomer is sterically favored over the *exo* isomer (Scheme 14).



Scheme 14. Adapted from Ref. [64].

A second, alternative process to obtain these complexes has been reported by Klazinga and Teuben [85]. The reactions of Cp_2MCl_2 with Grignard reagents (RMgCl) are reported to afford the complexes $Cp_2Nb(H)$(alkene). These reactions presumably proceed via the Nb(III) intermediate 'Cp_2NbR', in which β-H elimination occurs stereospecifically to give the alkene hydrides (Eq. (4)). Two equivalents of the Grignard reagent are required for this reaction. Presumably, one equivalent acts as a reducing agent [Nb(IV) → Nb(III)] and the other as the source of an alkyl ligand that β-H eliminates to generate the olefin–hydride complex.

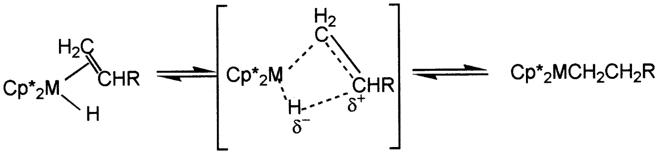
$$(C_5R_5)_2MCl_2 \quad + \quad 2\ R'MgX \longrightarrow (C_5R_5)_2M(H)(L) \tag{4}$$

M = Nb. R = Me; R' = C_2H_5, n-C_3H_7; L = C_2H_4, C_3H_6. [83]
R_5 = H_4SiMe_3; R' = PhC_2H_4; L = styrene. [64]

M = Ta. R = H; R' = n-C_3H_7, i-C_3H_7, n-C_4H_9, s-C_4H_9, n-C_5H_{11}. [85]
L = C_3H_6, C_4H_8 (1-butene), C_5H_{10} (1-pentene)

This method leads mainly to the *endo* isomer. In this field there have been recent reports [84] describing an alternative to this synthetic method. In fact, the starting niobium complex $[Cp'_2NbCl]_2$ ($Cp' = C_5H_4SiMe_3$) reacts with one equivalent of RMgX (R = Et, $CH_2CH_2C_6H_5$) to generate, at r.t. and in high yields, the corresponding olefin–hydride complexes $Cp'_2Nb(H)(\eta^2\text{-}RHC{=}CH_2)$ (R = H, C_6H_5) (*endo* isomer) by a highly steroselective β-elimination from the initially formed monoalkyl species $Cp'_2Nb(CH_2\text{–}CH_2R)$, which has not been detected. In order to obtain a firm understanding of the β-hydrogen elimination reaction, Doherty and Bercaw [83] carefully examined its microscopic reverse, the migratory insertion that occurs upon reaction of $Cp^*_2Nb(H)(CH_2{=}CHR)$ ($Cp^* = \eta^5\text{-}C_5Me_5$, with L = CO or CNMe) to afford $Cp^*_2Nb(CH_2{=}CHR)L$. Magnetization transfer experiments demonstrate a reversible migratory insertion ⇔ β-H elimination equilibrium, although the β-elimination rate constant is orders of magnitude greater than the insertion rate constant. The migratory insertion reactions of the series of *para*-substituted styrene complexes $Cp^*_2Nb(H)(CH_2{=}CHR)$ (R = Ph, *p*-$Me_2NC_6H_4$, *p*-$MeOC_6H_4$, *p*-MeC_6H_4, *p*-$CF_3C_6H_4$ [83]) in the presence of L were examined in a detailed kinetic and mechanistic study, and were found to be consistent with a four-center transition state in which bond making and breaking are concerted (Scheme 15). A small degree of positive charge builds up on the alkene C-β and negative charge on the migrating hydrogen, which is more consistent with its migration as a hydride H^-.

Closer examination of $Cp^*_2Nb(H)$(*exo*-$CH_2{=}CHR$) using spin-saturation transfer NMR experiments has provided compelling evidence for intermediates with agostic

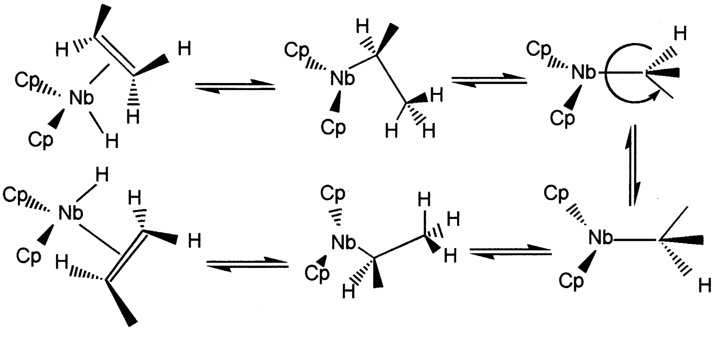


Scheme 15. Adapted from Ref. [83].

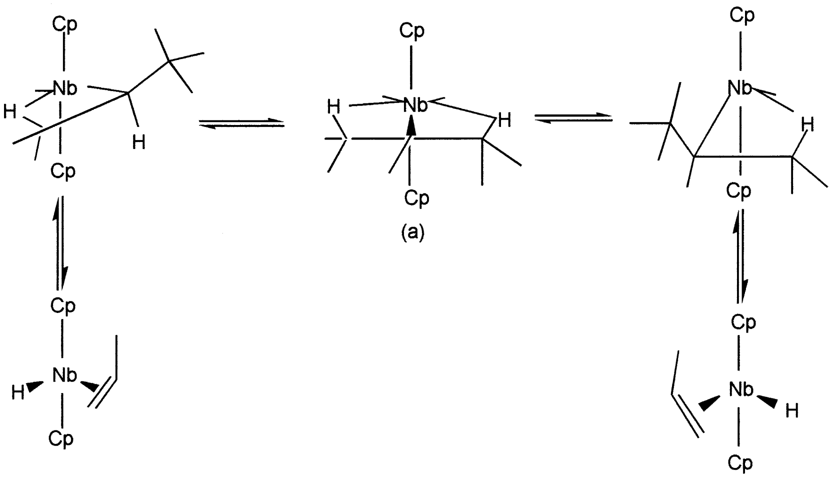
H–C bonding in the migratory insertion ⇔ β-H elimination reactions [86]. Initially, a mechanism for the exchange of NbH and the CH_2 hydrogens in *exo*-$Cp^*_2Nb(H)(CH_2{=}CHMe)$ was proposed based upon its rate being two orders of magnitude faster than the exchange of inequivalent Cp rings (Scheme 16) [87]. This mechanism involves a simple insertion followed by inversion about niobium and reinsertion to another *exo*-isomer.

However, in a later report by Green and co-workers [88], a new mechanism was proposed that involves an agostic alkyl ligand in the intermediate $Cp_2Nb(CHMe_2)$, which is formed upon insertion (Scheme 17). Thus, the exchange of NbH and the CH_2 hydrogens occurs by in-place rotation of this agostic alkyl intermediate. For the exchange of Cp ligands, the niobium center becomes planar as the alkyl group 'slides' across the face of the metal to form a complex (a) with a molecular plane of symmetry in which two agostic interactions (one from each Me group) are now present.

The mechanism of the formation of $Cp'_2NbH(PhCH{=}CH_2)$ ($Cp' = C_5H_4SiMe_3$) has been discussed [64] in terms of a model that implies a consecutive reaction with a reversible step and a first order dependence with respect to the precursor Cp'_2NbH_3, see Scheme 18. A value of 20.6 kcal mol^{-1} has been found for Ea. Likewise, studies on the insertion of styrene into the niobium–hydride bond on the mixture of *endo* and *exo* isomers of the aforementioned olefin–hydride niobocene complex were carried out by means of variable-temperature NMR studies using coalescence techniques.



Scheme 16. Adapted from Ref. [87].



Scheme 17. Adapted from Ref. [88].

4.4.2. *Reactivity studies*

The reactions [89] of $Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CH_2)$ and *endo*-$Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CHPh)$ with CS_2 in a 1:1 molar ratio were shown to be dependent on the experimental reaction conditions. Indeed, in an apolar solvent such as hexane or toluene, the alkyl/carbon disulfide complexes $Cp'_2Nb(Et)(\eta^2\text{-}CS_2\text{-}C,S)$ and $Cp'_2Nb(CH_2CH_2Ph)(\eta^2\text{-}CS_2\text{-}C,S)$ were formed exclusively. The carbon disulfide-promoted hydride–olefin insertion is the only process that occurs, and it gives rise exclusively to alkyl complexes. However, in polar solvents such as acetone, the dithioformato derivative $Cp'_2Nb(\eta^2\text{-}SC(H)S\text{-}S,S)$ and free olefin are generated along with small amounts of alkyl complexes (monitored by ^1H NMR spectroscopy).

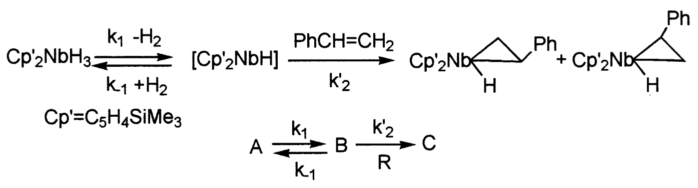
The reaction of niobocene olefin–hydride complexes with CO_2 and CO affords the alkyl–carbon dioxide and alkyl–carbonyl niobocene complexes, respectively (Eq. (5)).

$$(C_5R_5)_2Nb(H)(CH_2{=}CHR') + L \longrightarrow (C_5R_5)_2Nb(L)(CH_2CH_2R') \qquad (5)$$

$L = CO_2$ $R_5 = H_4SiMe_3$; $R' = H, C_6H_5, p\text{-}MeC_6H_4, p\text{-}MeOC_6H_4$. [84]

$L = CO$ $R_5 = H_4SiMe_3$; $R' = H, C_6H_5$. [84]

$R_5 = Me$; $R' = C_6H_5, p\text{-}MeNC_6H_4, p\text{-}MeOC_6H_4, p\text{-}MeC_6H_4, p\text{-}CF_3C_6H_4$. [83]

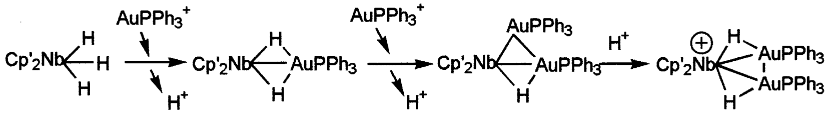


Scheme 18. Adapted from Ref. [64].

The niobocene olefin–hydride complexes react with a large excess of isocyanide to form alkyl isocyanide derivatives analogous to the CO adducts [83]. The reaction of *endo*-$Cp_2Ta(H)L$ [$L = C_3H_6$, C_4H_8 (1-butene)] with aryl and alkyl-isocyanides R′NC [$R' = 2,6\text{-}(CH_3)_2C_6H_3$, *cyclo*-$C_6H_{11}$, CH_3 and *t*-C_4H_9] gives the thermally stable isocyanide adducts of Cp_2TaR ($R = C_3H_7$, C_4H_9) [90]. The extraordinarily strong metal–isocyanide interaction leads to a nonlinear 'carbene-like' structure for these complexes and gives rise to the possibility of reactions at the nitrogen lone-pair of electrons. Complexes of type $Cp_2Nb(H)(CH_2{=}CHR)$ ($R = H$, CH_3, C_6H_5) react with propyne, 1-butyne, 2-butyne and phenylacetylene to give $Cp_2NbCH_2CH_2R$(alkyne) [91]. The resulting complexes prefer the *exo* geometry, which is in sharp contrast to the *endo* preference of the starting materials. Bulky 1-alkynes such as 3,3-dimethyl-1-butyne, (trimethylsilyl)acetylene and diphenylacetylene behave in a different manner and gave rise to the formation of hydridoniobocene complexes of the type $Cp_2Nb(H)$(alkyne) with *exo* geometry. $Cp_2Ta(H)$(alkene) complexes also react with alkynes in a similar manner. A recent report [92] has described the reactions of $Cp_2Ta(H)(C_2H_4)$ with perflouro-*n*-butyl iodide or perfluorobenzyl iodide, which cleanly yield the iodo(ethylene) complex $Cp_2Ta(C_2H_4)I$ together with the hydrofluorocarbons $CF_3CF_2CF_2CF_2H$ and $C_6F_5CF_2H$, respectively. In sharp contrast, reactions of $Cp_2Ta(H)(C_2H_4)$ with perfluoro-*iso*-propyl iodide or pentafluorophenyl iodide cleanly afford the isomeric iodo(ethylidene) complex $Cp_2Ta(CHCH_3)I$.

5. Heterobimetallic complexes containing cyclopentadienyl–hydride niobium- and tantalum moieties

The first compound containing a cyclopentadienyl hydride niobium- or tantalum-transition metal bond, whose characteristic structure has been determined, is the niobium complex $Cp_2(CO)Nb(\mu\text{-}H)Zn(BH_4)_2$ [93]. This compound was prepared by reduction of $NbCl_5$ with sodium cyclopentadienide and zinc powder in THF under a CO atmosphere at r.t., followed by treatment with $NaBH_4$. The geometry of the molecule shows a mirror plane containing the Nb, Zn, H and C (CO) atoms. The plane relates the two C_5H_5 rings and two BH_4 groups to each other. The large Zn…C(CO) (2.90 Å) and a practically linear structure of the Nb–CO fragment are indicative of the absence of a bond interaction between the carbonyl group and the Zn atom. The Nb–Zn bond (2.829 Å) should be described as a dative interaction $Nb \rightarrow Zn$. There is another complex $[\{Cp_2NbH_2\}_2Zn]$, reported by Tebbe in 1973, obtained as the sole product of the reaction between Cp_2NbH_3 and $ZnEt_2$ even when an excess of the latter reagent was employed [7b]. A structure with bridges of hydrogen atoms has been proposed for this compound. Although Cp_2NbH_3 reacts with $ZnEt_2$ to give a well-defined product, the reaction of the tantalum analogs resulted only in the formation of a loose adduct. Boersma and coworkers have carried out several reactions between Cp_2MH_3 ($M = Nb$, Ta) and Cp_2Zn, which gives a convenient starting material for the preparation of cyclopentadienylzinctransition metal compounds. It reacts smoothly with transition metal hydrides, forming direct zinc–metal bonds, under conditions where dialkylzinc compounds either fail to react or react very slowly [94,95]. When the reaction of Cp_2NbH_3 and Cp_2Zn is carried out in benzene, the use of an excess of the hydride niobocene resulted in the formation of the known compound reported by Tebbe, while with an excess of the Zn reagent, $[Cp_2NbH\{ZnCp\}_2]$ was formed. In THF as the solvent, $[Cp_2NbH_2ZnCp]$ was isolated as the sole product, whether an equimolar amount or an excess of Cp_2Zn was used. An X-ray diffraction study was carried out for this compound. The molecule resembles that of Cp_2NbH_3 with the central hydrogen atom replaced by a CpZn group [94]. A similar structure has been assigned to the tantalum analogs [95]. Meanwhile, Tebbe obtained $[\{Cp_2NbH_2\}Zn]$ as the sole reaction product, and evidence that the reactivity of Cp_2Zn is greater than that of $ZnEt_2$ appears from the fact that it is able to effect the substitution of a second hydrogen atom to yield $[Cp_2NbH\{ZnCp\}_2]$. This formula was corroborated by the isolation and structural characterization of the tantalum analog, which was isolated in the *transoid* and *cisoid* isomeric forms. The *transoid* isomer was converted irreversibly and completely into the *cisoid* isomer when a benzene solution was heated at 50°C for 3 h [95]. Pasynskii and coworkers have also prepared $[\{Cp_2(CO)Nb(\mu\text{-}H)_2\}_2M(CO)_4]$ (M = Mo, W) by the reaction of $Cp_2Nb(CO)H$ and $Ni(CO)_4$ and $M(CO)_6$ (M = Mo, W, respectively). In the molecular structures of these complexes the large Nb...Ni [3.218(2) Å], Nb...Mo [3.549(2) Å] and Nb...W [3.565(2) Å] distances show the weakening or even the absence of a direct niobium-transition metal bond interaction [96]. On the other hand, $Fe(CO)_5$ reacts rapidly with Cp_2NbH_3 even at r.t., to give the complex $[Cp_2(CO)Nb(\mu\text{-}H)M(CO)_3]$ [97]. When a mixture in THF of Cp_2NbH_3 and $M(CO)_6$ (M = Cr, Mo, W) is irradiated using a mercury lamp for 4 h, the complexes $[Cp_2(CO)Nb(\mu\text{-}H)M(CO)_5]$ (M = Cr, Mo, W) were formed [98]. The X-ray crystal study for the Cr derivative shows a bridging hydride between both metal centers, but the Nb–Cr distance [3.452(2) Å] indicates the absence of a direct metal–metal bond. These compounds can be viewed as containing three-center, two-electron Nb–H–M bonds, with the 18-electron moieties $Cp_2(CO)NbH$ effectively acting as a two-electron donor to the coordinatively unsaturated $M(CO)_5$ fragment. The tantalum analogs have also been reported by the reaction of $Cp_2TaH(CO)$, as a two-electron donor, with the Lewis acid organometallic fragments $M(CO)_5$ (M = Cr, Mo, W) or $CpMn(CO)_2$ [99]. Also, when a mixture in toluene of Cp_2NbH_3 and $[Mn_2(CO)_{10}]$ is irradiated for 50 min. using a fluorescent lamp ($\lambda_{max} = 3600$ Å), the ionic compound $[\{Cp_2(CO)Nb\}_2(\mu\text{-}H)]^+[Mn(CO)_5]^-$ was obtained. The cation should be described as the result of the protonation reaction on the dimer of two 17-electron fragments $[Cp_2(CO)Nb\text{–}Nb(CO)Cp_2]$ [98,100]. In contrast, when the same reaction is carried out with Cp_2TaH_3, the neutral complex $[Cp_2(CO)Ta(\mu\text{-}H)Mn_2(CO)_9]$ is isolated. The details about the sequence leading to one compound or the other are still unclear [98]. There is another cyclopentadienyl hydride niobium compound exhibiting an Nb–Nb bond whose crystal structure was determined by Guggenberger [101]. The complex was described as the result of the reduction reaction of Cp_2NbCl_2 with Na amalgam in THF. The compound Cp_2NbH_3 reacts with potassium hydride for



Scheme 19. Adapted from Ref. [105].

3 days in THF solution at r.t. to give an orange precipitate of $[K][Cp_2NbH_2]$ and this compound is then treated with a suspension of ytterbium diiodide in 1,2-dimethoxyethane, which must contain a trace of diglyme, at r.t. for 12 h to yield the compound $[\{NbCp_2H\}_2Yb{\cdot}diglyme]$ [102,103]. The X-ray crystal structure determination for this compound shows a central Nb–Yb–Nb core, with an Nb–Yb distance that lies between the sum of the Slater atomic radii and the sum of the metallic radii. In addition, there are two bridging hydrogens located symmetrically on each side of the Nb–Yb vector and these bridging hydrogens and the Nb and Yb atoms lie in a plane. Each Nb bears two Cp groups that are bent away from the Yb. The complete molecule has two-fold rotational symmetry about the $Yb{-}O(CH_2CH_2OCH_3)_2$ bond. Fajardo and coworkers reported, in a preliminary communication [104], the synthesis and structural characterization of the mixed metal cluster cation $[Nb(\eta^5\text{-}C_5H_4R)_2(AuPPh_3)_2]^+$ (R = H, $SiMe_3$) as the PF_6^- or ClO_4^- salts. In that communication they report the first examples of triangular '$NbAu_2$' metal frameworks with X-ray evidence for the metal–metal bonds. The complexes represented a new class of heteronuclear niobium–gold clusters. The metal framework, located on the reflection plane of the two cyclopentadienyl groups, consists of a triangle with rather similar and large [2.9139(8) Å and 2.9098(8) Å] Nb–Au bond distances. In the X-ray diffraction study the two hydride ligands were not located in the final structure. Several years later, the cationic compound was reported as a model of a protonation reaction with $[Au(PPh_3)]^+$ on Cp''_2NbH_3 and in this case the hydrides were found [105]. Whatever the stoichiometry {molar ratio $[Au(PPh_3)]^+$:complex, 1:1 or 2:1} or reaction conditions employed only the compound $[\{Cp_2Nb(\mu\text{-}H)_2\{Au(PPh_3)_2\}]^+$ was obtained. The different steps involved in the formation of this cationic complex are proposed in Scheme 19.

It has also been reported [105] that when $[Au\{N(SiMe_3)_2\}(PPh_3)]$ was used as an alternative gold reagent in order to avoid the final protonation process, the reaction with Cp'_2NbH_3, in a hydrocarbon solvent and at r.t. yielded a very air-sensitive product that was characterized as the raft cluster $[Au_3Nb_3(\mu\text{-}H)_6\{\eta^5\text{-}C_5H_4(SiMe_3)\}_6$. The structure contains a gold triangle surrounded by three Cp'_2Nb groups and six bridging hydrides. MO calculations indicate a striking electronic stabilization of this geometry [22].

The cationic complexes $[\{Nb(\eta^5\text{-}C_5H_3RR')_2H_3\}_2Au]^+$ (R = R′ = H; R = H, R′ = $SiMe_3$; R = R′ = $SiMe_3$) were synthesized, as mentioned previously, upon addition of '$[Au(THT)][PF_6]$', prepared in situ from [AuCl(THT)] and $TlPF_6$, to $[Nb(\eta^5\text{-}C_5H_3RR')_2H_3]$ in THF [21b]. The crystal structure of one of these cationic complexes showed that the metal core consists of an almost linear arrangement of Nb, Au and Nb atoms [Nb–Au–Nb angle 175.92(2)°]. The coordination around the Au atom is intermediate between tetrahedral and square planar. This geometry and the locations of the hydrides suggest a significant narrowing of the distance between one of the bridging hydrides and the terminal [17]. On the other hand, the reaction of Cp_2NbHL ($L = P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$) with $[Au(PPh_3)][PF_6]$, obtained in situ from $[Au(PPh_3)Cl]$ and $TlPF_4$, in THF solution and at r.t. leads to the mixed-metal Nb–Au complexes $[Cp'_2L(\mu\text{-}H)(AuPPh_3)][PF_6]$, where the niobium–hydrogen–gold interaction can be considered to occur through a three-center two electron bond. The authors proposed an additional niobium–gold interaction [49]. The cationic complexes $[\{Cp'_2Nb(CO)(\mu\text{-}H)\}_2M]^+$ ($M = Cu, Ag, Au$) are the result of the reaction of $Cp'_2Nb(CO)H$ with $[Cu(MeCN)_4][BF_4]$, $[Cu(PPh_3)Cl]/TlPF_6$, $AgBF_4$, $[Ag(PPh_3)Cl]/TlPF_6$ or $[Au(THT)Cl]/TlPF_6$. In these complexes, the coinage cation is only linked to the hydride of each niobium center [23]. The most important result of this study is that the formation of the adducts essentially involves binding of the hydride of a niobium moiety to the Lewis acidic cation M(I). In addition, a weak interaction between the Lewis acid and CO is present, at least in the case of copper, with a pseudotetrahedral geometry around the copper. Nevertheless, the same reaction with $[AuPPh_3Cl]/TlPF_6$ leads to the complex $[\{NbCp'_2(CO)\}(\mu\text{-}H)(AuPPh_3)][PF_6]$, and this cationic complex contains one niobium atom linked to a '$(AuPPh_3)$' fragment. The nature of this bonding and the geometry around the gold atom are, however, unknown [23].

Acknowledgements

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