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On the insertion processes of unsaturated molecules into the Nb–X σ-bond of "Cp'_2NbX" moieties ($Cp' = \eta^5$-$C_5H_4SiMe_3$; X = H, C, P)

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Dedicated to Professor Gerhard Erker on occasion of his 60th birthday.

Abstract

In this article, we have reviewed a series of insertion processes of different types of unsaturated reagents, namely carbon monoxide, carbon dioxide, isocyanates, isothiocyanates, isonitriles, alkenes and activated alkynes, in the Nb–X σ-bond, X = H, C and P, of "Cp'_2NbX" moieties, $Cp' = \eta^5$-$C_5H_4SiMe_3$.

Keywords: Niobocene; Insertion

1. Introduction

The insertion reaction represents one of the fundamental processes of organometallic chemistry and continues to attract considerable interest, especially in terms of the stereochemistry of the resulting products and in terms of reaction mechanisms [1].

In broad terms, two types of insertion reactions can be discerned, namely migratory and nonmigratory insertions. Migratory insertions, that are better known, require a vacant site at the metal center or a labile ligand to be easily replaced by the incoming reagent and should be *cis* stereospecific processes. In contrast, complexes that are coordinatively saturated and inert towards substitution cannot undergo migratory insertion. However, these types of derivatives can insert activated molecules or unsaturated molecules, producing new complexes of varying stereochemistry, through both *cis* or *trans* sterospecific processes. These reactions may be called nonmigratory insertions reactions.

This article covers some of the results of our studies on the insertion processes of different types of unsaturated molecules, namely CO, CO_2, isocyanates, isothiocyanates, isonitriles, olefins, activated alkynes, in the Nb–X σ-bond of the formally 16-electron moieties "Cp'_2NbX" ($Cp' = \eta^5$-$C_5H_4SiMe_3$; X = H, C, P).

2. Reactivity of the Nb–H bond in niobocene derivatives

The formation of the metal-hydride bond is considered a fundamental chemical step in several catalytic cycles and frequently leads to reactive intermediates [1]. In this section the reactivity of the hydride niobocene "Cp'_2NbH" moiety ($Cp' = \eta^5$-$C_5H_4SiMe_3$ throughout this review) toward several unsaturated molecules will be reviewed. Indeed, many examples have been described by us and others 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 a specific group of insertion processes with alkynes and alkenes will then be described.

2.1. Insertion processes with heterocumulenes

Insertion reactions involving heterocumulenes, like those of carbon disulfide, isocyanate or isothiocyanate,

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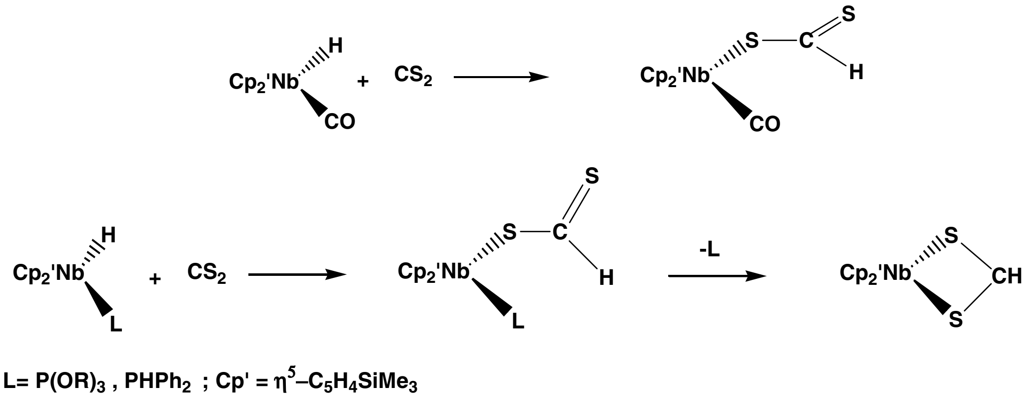
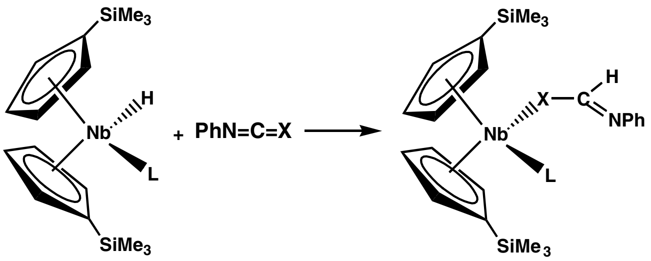


Scheme 1.

are particularly interesting because they allow the modeling of the insertion reactions of carbon dioxide, a process that constitutes an attractive goal in the field of organometallic chemistry.

We have studied the reactivity of complexes $Cp'_2Nb(H)(L)$, (L = CO, $P(OR)_3$, $PHPh_2$) [2], with CS_2 and found that the process proceeds with the expected insertion of the heterocumulene into the Nb–H bond to give a dithioformate ligand, S(S)CH (Scheme 1), and that the nature of the products is dependent on the type of L. In fact, when L = CO the new ligand gives η^1-dithioformate coordination, whereas when L = $P(OR)_3$ or $PHPh_2$ the η^2-dithioformate coordination mode is present. In the latter cases, an initial η^1-dithioformate intermediate complex is probably formed, followed by the loss of phosphite or phosphine to give the final η^2-dithioformate ligand – behavior that is unusual in this type of insertion process.

When the heterocumulene is isocyanate (RNCO) or isothiocyanate (RNCS) the insertion reaction into the Nb–H bond gave the formamide- or thioformamide-containing complexes $Cp'_2Nb(\eta^1$-X-XC(H)NR)(L), X = O, S; L = CO, CNR [3] (Scheme 2).



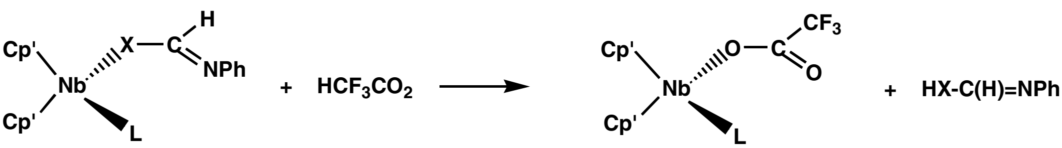
Scheme 2.

These complexes have been studied by different structural techniques. For example, their ^1H and ^{13}C NMR spectra show four and five signals, respectively, for the cyclopentadienyl rings, a finding consistent with a lack of symmetry in their structures. The subsequent protonation of $Cp'_2Nb(\eta^1$-X-XC(H)NR)(L) complexes using CF_3-COOH yielded the trifluoroacetate complexes $Cp'_2Nb(\eta^1$-O-O(O)CCF$_3$)(L) and the corresponding imine derivatives, namely HOC(H)=NR and HSC(H)=NR (Scheme 3).

Finally, the thermal behavior of the formamide-containing complex in which L = CO and X = O was studied. In the process an evolution of CO took place, resulting in the isolation of a η^2-formamide complex Cp'_2Nb-(η^2-O, N-OC(H)NPh).

The interaction of the trihydride niobocene Cp'_2NbH_3 with carbon dioxide was investigated because metalloformate M–CO(O)H units derived from carbon dioxide insertion into M–H bonds are known to be involved in the catalytic hydrogenation of that molecule to give formic acid and its derivatives [4]. The complex Cp'_2NbH_3 reacted with CO_2 to give the formate complex $Cp'_2Nb(\eta^2$-O, O-O(O)CH) [5] (Scheme 4), which can also be formed from the electroreduction of Cp'_2NbCl_2 in the presence of formic acid.

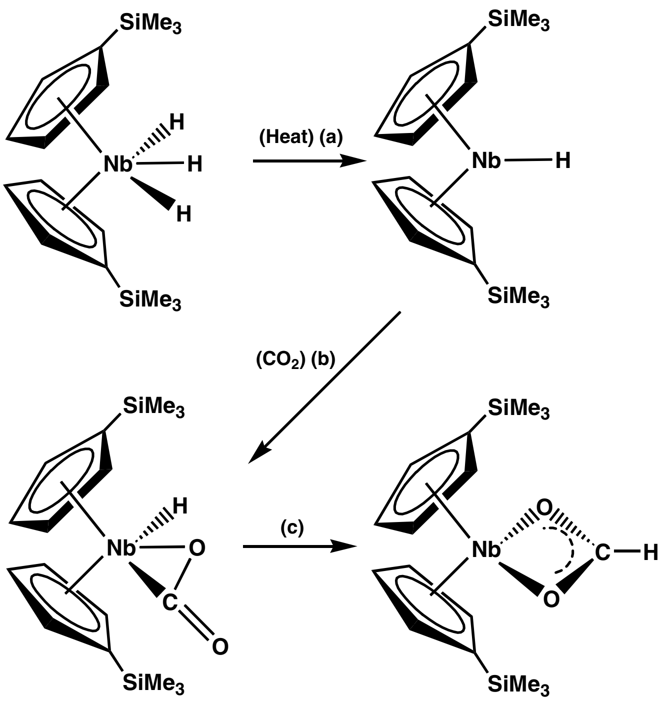
The isolation of $Cp'_2Nb(\eta^2$-O, O-O(O)CH) as the final product from this reaction can be understood in terms of Scheme 5. Step (a) corresponds to the elimination of H_2 and the formation of a very reactive 16-electron monohydride niobocene species, which has previously been proposed in several processes [6]. Coordination of CO_2 to



Scheme 3.

$$Cp_2'NbH_3 + CO_2 \rightarrow Cp_2'Nb(\eta^2\text{-O,O-O(O)CH})$$

Scheme 4.



Scheme 5.

this unsaturated species to give an 18-electron hydride-carbon dioxide intermediate is suggested in step (b), although experimental data to confirm this suggestion is lacking since all attempts to detect it, including several ^{1}H and ^{13}C NMR experiments, were unsuccessful, probably because under the required experimental conditions, i.e. heating at 60 °C, the subsequent step would be too fast and thus prevent detection. The final step (c) corresponds to the insertion of the coordinated CO_2 into the Nb–H bond to give the formate ligand [7]. Nicholas and co-workers [8] have published data that confirm the formation of a hydride-carbon dioxide tantalocene intermediate at −40 °C as well as the subsequent insertion to give formate-tantalocene derivatives. It is worth noting that precoordination of CO_2, followed by a subsequent insertion process into an M–H bond were discounted in several cases [9], and as far as we are aware the proposed mechanism was confirmed for the first time in the aforementioned tantalocene example. Therefore, the formation of complex $Cp'_2Nb(\eta^2\text{-O,O-O(O)CH})$ through the steps outlined in Scheme 5 was proposed with caution, since an alternative pathway involving direct insertion of CO_2 into the Nb–H bond without prior coordination cannot be excluded.

Reactivity studies on $Cp'_2Nb(\eta^2\text{-O,O-O(O)CH})$ have been carried out. The reaction with CS_2 or the π-acids CO and $CN(2,6\text{-}C_6H_3Me_2)$ leads to the transformation from bidentate to monodentate formate as a consequence of coordination of the incoming ligand (see Scheme 6).

$$Cp_2'Nb(\eta^2\text{-O,O-O(O)CH}) + L \rightarrow Cp_2'Nb(\eta^1\text{-O,-O(O)CH})(L)$$

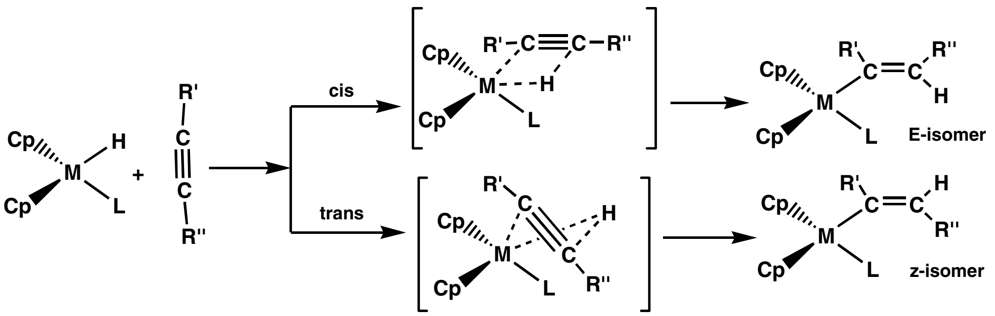
Scheme 6.

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 a strong π-acceptor is necessary to break an Nb–O bond and to transform the formate from a bidentate into a monodentate system. Alternatively, the complex in which L = CO can be prepared in the reaction of the hydrido complex $Cp'_2Nb(H)(CO)$ with CO_2 through an insertion into the Nb–H bond. Infrared and, in particular, NMR spectroscopy have proved to be useful for the characterization of the formate niobocene complexes. For instance, the CO_2^- stretching frequencies are usually the most prominent feature of the IR spectra and attention has been focused on those signals. The most common approach has been to relate the values of Δ [the separation between $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$] with the mono- or bidentate character of the ligands [10]. The IR spectrum of $Cp'_2Nb(\eta^2\text{-O,O-O(O)CH})$ shows two bands at 1638 and 1545 cm^{-1} and these correspond to $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$, respectively; the value $\Delta = 93$ cm^{-1} is significantly lower than the 'ionic' value, $\Delta = 201$ cm^{-1}, which indicates that the formate ligand in $Cp'_2Nb(\eta^2\text{-O,O-O(O)CH})$ acts as a bidentate group. Moreover, the ^{1}H and ^{13}C NMR data confirmed the bidentate coordination. In fact, the observation of two and three signals for each cyclopentadienyl ring in the ^{1}H and ^{13}C NMR spectra, respectively, indicates the presence of a symmetrical environment. Furthermore, the IR spectra of complexes $Cp'_2Nb(\eta^1\text{-O-O(O)CH})(L)$ showed $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$ to have Δ values of 332, 318 and 318 cm^{-1}, respectively, which are consistent with the presence of a monodentate formate ligand. Once again, the NMR data confirmed this situation; thus, the ^{1}H and ^{13}C NMR spectra showed four and five signals, respectively, for each cyclopentadienyl ring, which is consistent with a lack of symmetry.

Complex $Cp'_2Nb(\eta^2\text{-O,O-O(O)CH})$ was also prepared by reaction of $Cp'_2Nb(H)(PHPh_2)$ [2b] with CO_2. Insertion of CO_2 into the Nb–H bond probably results initially in the formation of a η^1-formate intermediate $Cp'_2Nb(\eta^1\text{-O-O(O)CH})(PHPh_2)$. This complex rapidly evolves through the elimination of phosphane (due to a substitution reaction of phosphane by the noncoordinated oxygen atom) to give the η^2-formate complex. This behavior was previously found in the reactions of some complexes of the type $Cp'_2Nb(H)(L)$ with CS_2 [2a].

2.2. Insertion processes with activated alkynes

The insertion of alkynes into transition metal–hydrogen bonds is a key elementary step in catalytic polymerization and hydrogenation processes of these unsaturated



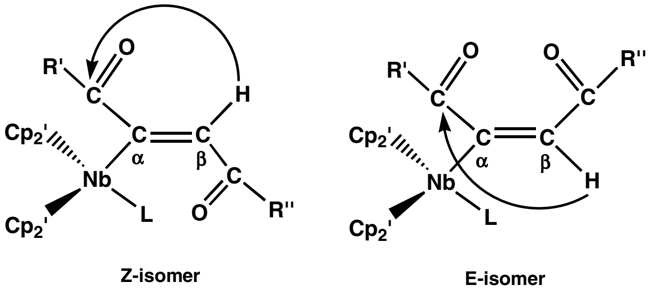
Scheme 7.

molecules [1]. In recent years, the stereochemistry and mechanism involved in the insertion process have received considerable attention [11]. In the process *cis*- and *trans*-insertion yield the (*E*)-alkenyl and (*Z*)-alkenyl products, respectively, and 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 (Scheme 7). 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 [12] 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 [13].

However, our hydride-isocyanide complexes $Cp'_2Nb(H)(CNR)$ ($R = {}^tBu$, Cy, 2,6-$C_6H_3Me_2$) reacted with several activated alkynes to afford the corresponding alkenyl-isocyanide complexes $Cp'_2Nb(CNR)(C(R'){=}\,CH(R''))$ through a stereospecific *cis*-insertion resulting in the formation of (*E*)-alkenyl products [14].

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 7, which is favored by steric factors. In the same reaction for $Cp'_2Nb(H)(CO)$ 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 structural characterization of the different alkenyl niobocene complexes was carried out by IR and NMR spectroscopy. In NMR spectroscopy the value of the vicinal coupling constant of the alkenyl protons with the carbonyl carbon atom of the R-carbon has been used as a useful tool to establish the (*E*)- or (*Z*)-stereochemistry for the alkenyl group (Scheme 8).



Scheme 8.

The results obtained in the reaction of Cp'_2NbH_3 with activated alkynes (Scheme 9) were particularly interesting [14]. In fact, this complex reacted with activated alkynes, such as $RO_2CC{\equiv}CCR'$, to afford new hydride-olefin complexes $Cp'_2Nb(H)(\textit{trans}\text{-}\eta^2\text{-}RO_2CCH{=}CHR')$.

This behavior is surprising because reactions of this type between trihydride metallocenes and alkynes are well known and generally give rise to alkyne-hydride metallocenes [15].

In order to explain the formation of these complexes, a stereospecific *trans*-insertion to give a dihydride alkenyl intermediate is suggested as the first step, followed by an intermolecular rearrangement that leads to the final hydride-olefin complexes (Scheme 10).

The structural characterization of these niobocene complexes was carried out by spectroscopic and X-ray diffraction studies. ^1H and ^{13}C NMR spectra exhibit eight and 10 resonances for the proton and carbon atoms, respectively, for the two cyclopentadienyl ligands, indicating that they are inequivalent, and this behavior is in agreement with the structural disposition (vide infra) observed for these complexes where the olefinic carbon atoms are coplanar with the niobium and hydride atoms in such a way that their substituents (in a *trans*-disposition) are situated in a

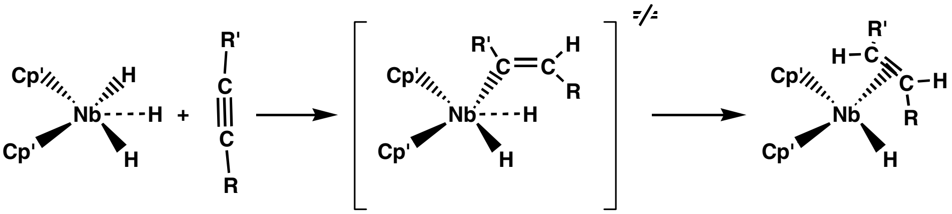
$$Cp_2'NbH_3 + RC{\equiv}CR' \rightarrow Cp_2'Nb(H)(\eta^2\text{-}RC(H){=}C(H)R'')$$

$$R = R' = CO_2Me$$

$$R = R' = CO_2{}^tBu$$

$$R = CO_2Mr,\ R' = H$$

Scheme 9.



Scheme 10.

plane orthogonal to that containing the aforementioned atoms. This structural conformation leads to the presence of two resonances for the inequivalent $SiMe_3$ groups. Finally, the presence in the ^1H NMR spectra of AB spin systems for the olefinic protons must also be emphasized.

2.3. Insertion processes with alkenes

The insertion of olefins into metal-hydride bonds [16] and its microscopic reverse, β-elimination, are very common steps in industrial catalytic reactions such as olefin isomerization, hydrogenation, and hydroformylation.

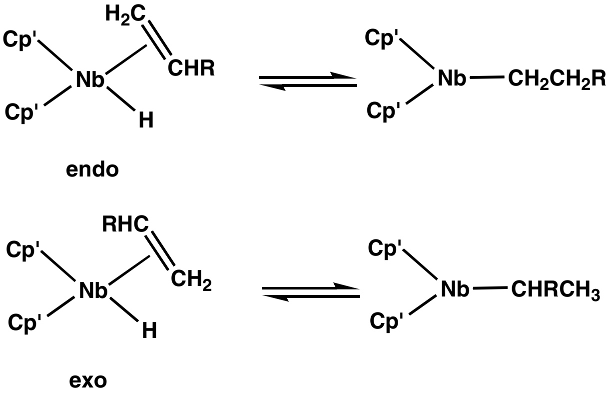
The hydride-olefin complex $Cp'_2Nb(H)(\eta^2\text{-}PhCH{=}CH_2)$ was synthesized [17a] when Cp'_2NbH_3 was reacted with 2 equivalents of styrene. The reaction proceeds by thermal elimination of H_2 followed by olefinic coordination to the "Cp'_2NbH" intermediate. The mechanism for the formation of $Cp'_2Nb(H)(\eta^2\text{-}PhCH{=}CH_2)$ has been discussed in terms of a model that involves a consecutive reaction with a reversible step and a first order dependence with respect to the precursor Cp'_2NbH_3. A value of 20.6 kcal mol^{-1} has been found for Ea (Scheme 11).

This complex was isolated as a mixture of *endo* and *exo* isomers in almost equal proportion. However, it has been pointed out that the *endo* isomer is sterically favored over the *exo* isomer, although the *endo* isomer can be selectively prepared by reacting Cp'_2NbCl_2 with 2 equivalents of $PhCH_2CH_2MgBr$.

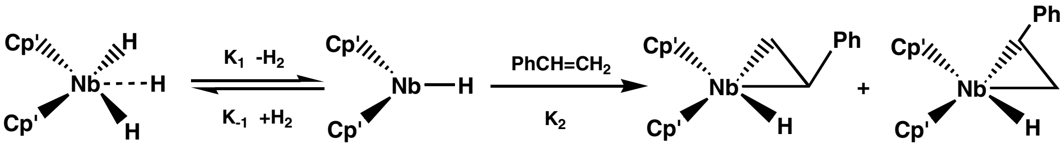
Likewise, studies on the insertion of styrene into the niobium-hydride bond in the mixture of *endo* and *exo* isomers of the aforementioned olefin-hydride niobocene complex (Scheme 12) were carried out by means of variable-temperature NMR studies using coalescence techniques. When the temperature was raised, an exchange of the hydride ligand with the hydrogen atoms of the olefin was found to take place.

In a continuation of this work, the analogous niobocene-hydride-ethylene species $Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CH_2)$ was prepared by the reaction of $[Cp'_2NbCl]_2$ with 1 equivalent of EtMgBr, and an exhaustive variable-temperature NMR study of the hydride-olefin insertion β-elimination equilibrium was performed [17b].

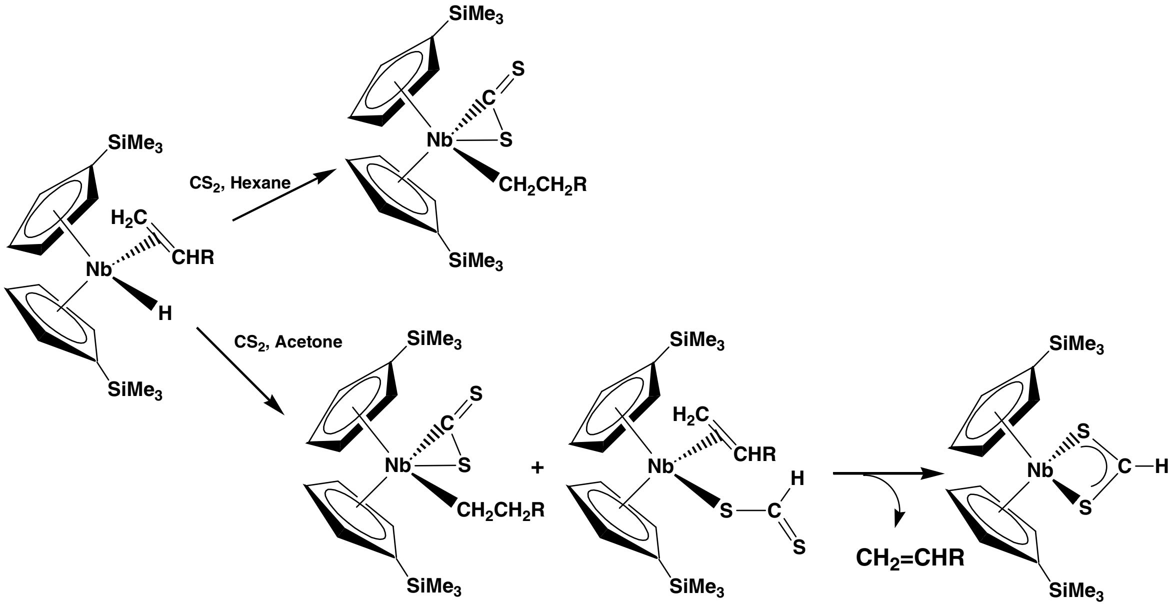
The reactions of $Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CH_2)$ and *endo*-$Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CHPh)$ with CS_2 in a 1:1 molar ratio were shown to be dependent on the experimental reaction conditions [18]. Indeed, in apolar solvents such as hexane or toluene, the alkyl/carbon disulfide complexes $Cp'_2Nb(Et)(\eta^2\text{-}CS_2)$ and $Cp'_2Nb(CH_2CH_2Ph)(\eta^2\text{-}CS_2)$ were formed exclusively. The carbon disulfide-promoted hydride-olefin insertion is the only process that occurs, and this gives rise exclusively to alkyl complexes. However, in polar solvents, such as acetone, the dithioformate derivative $Cp'_2Nb(\eta^2\text{-}S,S\text{-}S(S)CH)$ and free olefin are generated along with small amounts of alkyl complexes (Scheme 13) (monitored by ^1H NMR spectroscopy). The dithioformate-niobocene species results from the insertion of CS_2 into the Nb–H bond in the starting material to produce a η^1-dithioformate-olefin intermediate, which was detected by ^1H NMR, followed by an elimination of olefin to give a η^2-dithioformate ligand. This latter behavior has previously been found in the reaction of $Cp'_2Nb(H)(L)$ with CS_2 [6].



Scheme 12.



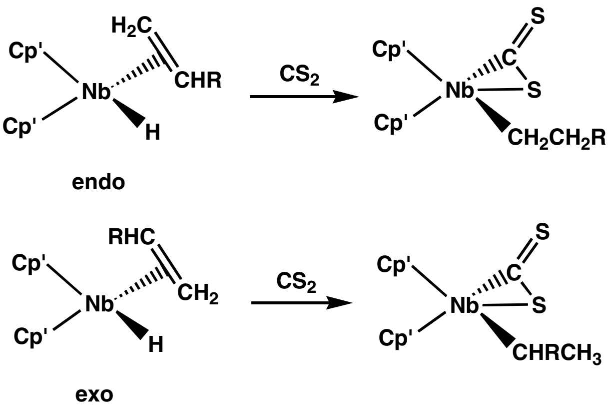
Scheme 11.



Scheme 13.

Interestingly, the addition of CS_2 to a mixture of both the *endo* and *exo* styrene isomers, generated by heating a solution of the pure *endo* isomer for several days, resulted in complex $Cp'_2Nb(CH_2CH_2Ph)(\eta^2\text{-}CS_2)$ being isolated as the only product, a surprising result since we would expect a mixture of two alkyl isomers $Cp'_2Nb(CH_2CH_2Ph)(\eta^2\text{-}CS_2)$ and $Cp'_2Nb(CHPhCH_3)(\eta^2\text{-}CS_2)$ to be formed (Scheme 14). The CS_2 is probably trapping the insertion intermediate arising from the *endo* isomer faster than the insertion intermediate arising from the *exo* isomer, thus the primary alkyl-containing complex $Cp'_2Nb(CH_2CH_2Ph)(\eta^2\text{-}CS_2)$ would be the expected kinetic product [19].

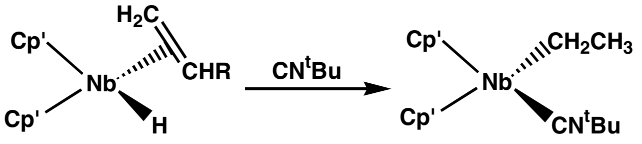
The reaction of niobocene olefin-hydride complexes with CO_2 and CO affords the alkyl-carbon dioxide and alkyl-carbonyl niobocene complexes, respectively [17] (Scheme 15).



Scheme 14.

$$(C_5R_5)_2Nb(H)(\eta^2\text{-}CH_2{=}CHR') + L \rightarrow (C_5R_5)_2Nb(H)(CH_2CH_2R')$$
$$(L = CO, CO_2)$$

Scheme 15.



Scheme 16.

The aforementioned hydrido(ethylene) complex $Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CH_2)$ was found to react [20] slowly at room temperature with one equivalent of isocyanides to give the ethyl isocyanide derivatives $Cp'_2Nb(CH_2CH_3)(CNR)$. The isocyanide ligand promotes the insertion of the olefin into the niobium-hydride bond (Scheme 16). A second equivalent of isocyanide can undergo an insertion into the Nb–C bond of the ethyl group and this will be discussed in the following section of this report.

3. Reactivity of the Nb–C bond in niobocene derivatives

In the following sections, insertion precesses of CO, CO_2 and isocyanides into the niobium–carbon bond will be described. The isolobal relationship between carbon monoxide and isocyanide compounds suggests that similar types of reactivity can be expected.

3.1. Insertion processes with CO and CO_2

In an effort to perform a more in-depth study on the reactivity of the olefin-hydride complexes $Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CH_2)$ and $Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CHC_6H_5)$

toward carbon monoxide, toluene solutions of these complexes were heated under reflux under pressure with CO and this led to the isolation of acylniobocene species $Cp'_2Nb(CO)(\eta^1\text{-}C(O)CH_2CH_3)$ and $Cp'_2Nb(CO)(\eta^1\text{-}C(O)CH_2\text{-}CH_2C_6H_5)$ after appropriate workup (Scheme 17) [17]. Although cyclopentadienylacylniobium and -tantalum species arising from migratory insertion of alkylcarbonyl complexes have been claimed to participate as intermediates in different processes, neutral acylmetallocenes had not been isolated or characterized prior to this work.

The same complexes were obtained from the reaction of the alkyl complexes $Cp'_2Nb(CO)(R)$ ($R = CH_2CH_3$, $CH_2\text{-}CH_2C_6H_5$) with CO under similar experimental conditions.

Spectroscopic data are consistent with the proposed formulae for the acyl niobocene complexes. For example, the IR spectra contain an acyl C=O stretch at $1599\ cm^{-1}$, and although this value is lower than those reported for the previously discussed cationic acylniobocenes that contain a η^2-acyl (ca. $1620\ cm^{-1}$), a η^1-acyl coordination must be proposed in our complexes in order to attain an 18-electron configuration for the Nb(III) ion [21]. This represents an unusual situation because η^2-acyl coordination is very commonly encountered among the early transition metals [22].

Furthermore, reactions of the acyl niobocene complexes $Cp'_2Nb(\eta^1\text{-}C(O)CH_2CH_3)(CO)$ and $Cp'_2Nb(\eta^1\text{-}C(O)\text{-}CH_2\text{-}CH_2C_6H_5)(CO)$ with CF_3COOH in acetone as the solvent gave the corresponding aldehydes and the niobocene trifluoroacetate complex $Cp'_2Nb(\eta^1\text{-}O\text{-}O(O)CCF_3)(CO)$, a finding in agreement with the reaction shown in Scheme 18 [23].

3.2. Insertion processes with isocyanides

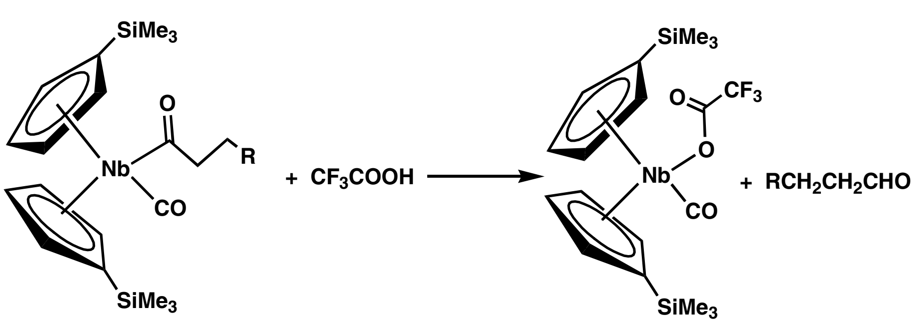
Following on from our studies on the first insertion reaction of CO into the niobium–carbon bond of alkylniobocene complexes, which gave the corresponding η^1-acyl derivatives, we considered the insertion processes by using isocyanide compounds [20]. The isolobal relationship between carbon monoxide and isocyanide compounds suggests that similar types of reactivity can be expected, although isocyanides are generally regarded as better σ donors and weaker π acceptors than carbon monoxide [24].

In contrast to the behavior observed in the synthesis of $Cp'_2Nb(CH_2CH_3)(CN^tBu)$ by the reaction of $Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CH_2)$ with CN^tBu [20], an equimolar amount of 2,6-dimethylphenyl isocyanide reacted at room temperature with $Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CH_2)$ to give initially the ethyl isocyanide derivative $Cp'_2Nb(CH_2CH_3)(CN\text{-}2,6\text{-}C_6H_3Me_2)$. This compound evolved rapidly at room temperature with the insertion of a second equivalent of the isocyanide ligand into the niobium–carbon bond to yield the neutral iminoacyl compound $Cp'_2Nb\{\eta^1\text{-}C\text{-}C({=}N\text{-}C_6H_3Me_2)(CH_2CH_3)\}(CN\text{-}2,6\text{-}C_6H_3Me_2)$ (Scheme 19).

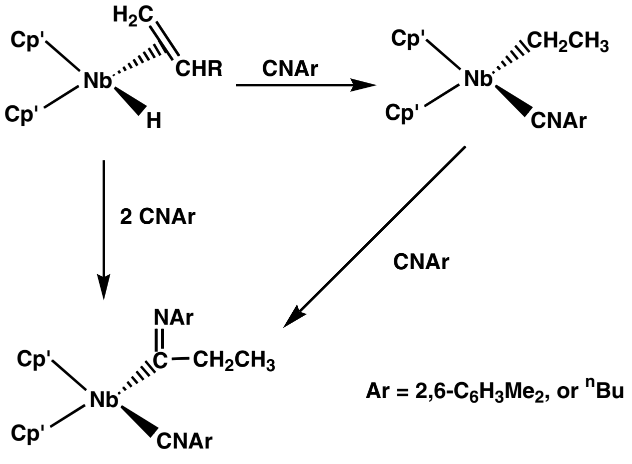
The isocyanide derivative $Cp'_2Nb(CH_2CH_3)(CN\text{-}2,6\text{-}C_6H_3Me_2)$ was characterized by ^1H NMR spectroscopy and typical resonances corresponding to the cyclopentadienyl, ethyl and isocyanide ligands were observed. The IR spectrum of the iminoacyl compound $Cp'_2Nb\{\eta^1\text{-}C\text{-}C({=}N\text{-}2,6\text{-}C_6H_3Me_2)(CH_2CH_3)\}(CN\text{-}2,6\text{-}C_6H_3Me_2)$ contained a band corresponding to the stretching mode $\nu(CN)$ of the linear isocyanide ligand at $2021\ cm^{-1}$. The $\nu(C{=}N)$ stretching frequency corresponding to the η^1-iminoacyl ligand was observed at $1657\ cm^{-1}$. NMR evidence supports the proposal that the iminoacyl ligand in this compound is coordinated in a η^1-fashion. The ^1H NMR resonance of the inserted methylene group of the ethyl ligand is displaced to lower field, $\delta = 2.35$ ppm, with respect to that observed in $Cp'_2Nb(CH_2CH_3)(CN\text{-}2,6\text{-}C_6H_3Me_2)$, $\delta = 0.81$ ppm. In the ^{13}C NMR spectrum a low field resonance, $\delta = 218.2$ ppm, was observed for the carbon of the terminal isocyanide ligand bonded to niobium. A second signal

$$Cp_2'Nb(H)(\eta^2\text{–}CH_2{=}CHR) + CO \xrightarrow[\Delta]{} Cp_2'Nb(CO)(\eta^1\text{-}C(O)CH_2CH_2R)$$

Scheme 17.



Scheme 18.



Scheme 19.

shifted to higher field, $\delta = 153.6$ ppm, was assigned to the carbon of the η^1-iminoacyl ligand. The previously reported cationic iminoacylniobium derivatives $[Cp'_2NbX(\eta^2\text{-C,N-C(=NPh)CHCHRPh})]^+$ (X = Cl, H, CH_3) [25] showed the signal attributed to the η^2-iminoacyl carbon in the range $\delta = 213$–219 ppm, which is consistent with the data reported for complexes of other early transition metals [26].

Further evolution of the iminoacyl compound $Cp'_2Nb\{\eta^1\text{-C-C(=N-2,6-}C_6H_3Me_2)(CH_2CH_3)\}(CN\text{-2,6-}C_6H_3Me_2)$ to give the coupling of the isocyanide and the η^1-iminoacyl groups to produce metallacyclic compounds was not observed [27].

Furthermore, the reaction of *n*-butyl isocyanide with $Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CH_2)$ also gave a mixture of products, namely the alkyl compound $Cp'_2Nb(CH_2CH_3)(CN^nBu)$ and the iminoacyl complex $Cp'_2Nb\{\eta^1\text{-C-C(=N}^nBu)(CH_2CH_3)\}(CN^nBu)$ (Scheme 19). An excess of isocyanide gave rise to further reactions that produced a mixture of products, which we were unable to identify.

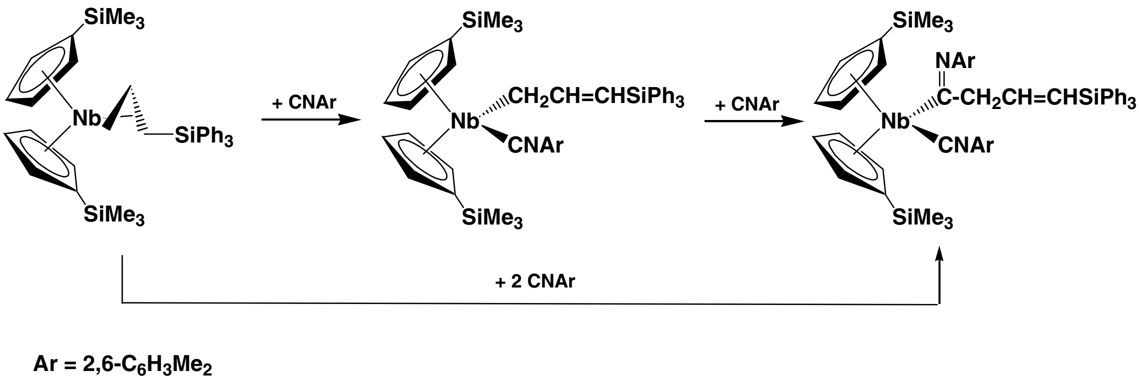
The allyl niobocene complex $Cp'_2Nb(\eta^3\text{-CHRCHCHR}')$ (R = R′ = $SiMe_2{}^tBu$) [20] did not react with 2,6-dimethylphenyl isocyanide at room temperature and at 80 °C the products from the reaction could not be identified. However, $Cp'_2Nb(\eta^3\text{-}CH_2CHCHSiPh_3)$ reacted with two equivalents of 2,6-dimethylphenyl isocyanide at room temperature to give initially the η^1-allyl isocyanide derivative $Cp'_2Nb(\eta^1\text{-}CH_2CH{=}CHSiPh_3)(CN\text{-2,6-}C_6H_3Me_2)$, which subsequently underwent an insertion reaction with a further isocyanide to give the iminoacyl derivative $Cp'_2Nb\{\eta^1\text{-C-}C(\text{=N-2,6-}C_6H_3Me_2)(CH_2CH{=}CHSiPh_3)\}(CN\text{-2,6-}C_6H_3Me_2)$ (Scheme 20).

In contrast, $Cp'_2Nb(\eta^3\text{-}CH_2CHCH_2)$ did not react with the aryl isocyanide at room temperature, and the reaction had to be carried out at 80 °C in order to obtain the corresponding η^1-iminoacyl compound $Cp'_2Nb\{\eta^1\text{-C-C(=N-2,6-}C_6H_3Me_2)(CH_2CH{=}CH_2)\}(CN\text{-2,6-}C_6H_3Me_2)$ (Scheme 21). Under these conditions the corresponding intermediate η^1-allyl derivative $Cp'_2Nb(\eta^1\text{-}CH_2CH{=}CH_2)(CN\text{-2,6-}C_6H_3Me_2)$ was not detected. The reaction of $Cp'_2Nb(\eta^1\text{-}CH_2CH{=}CH_2)(CN\text{-2,6-}C_6H_3Me_2)$ with an equimolar amount of aryl isocyanide gave the iminoacyl complex $Cp'_2Nb\{\eta^1\text{-C-C(=N-2,6-}C_6H_3Me_2)(CH_2CH{=}CH_2)\}(CN\text{-2,6-}C_6H_3Me_2)$ (Scheme 21).

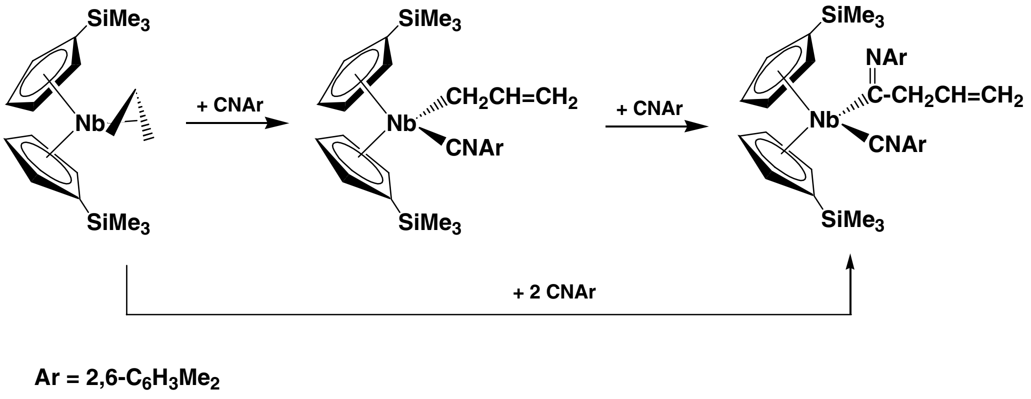
NMR spectroscopy allowed the relative ease of the insertion reactions of different isocyanide molecules to be established for the different niobium systems, and the following order was found: $CN^nBu > CN\text{-2,6-}C_6H_3Me_2 > CN^tBu$ for the isocyanide molecules and $Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CH_2) > Cp'_2Nb(\eta^3\text{-}CH_2CHCHSiPh_3) > Cp'_2Nb(\eta^3\text{-}CH_2CHCH_2)$ for the organometallic substrates.

As a continuation of our study into the insertion of isocyanides into the Nb–C bonds of niobocene complexes, we found [28] an unexpected type of reactivity in phosphido niobocene complexes containing the isocyanide ancillary ligand $CN\text{-2,6-}C_6H_3Me_2$ on reaction with electron-poor alkynes. A cycloaddition process gave rise to novel five-membered heteroniobacycles. Examples of heterometallacycles of late-middle transition metals from cycloaddition processes involving alkynes are known [29].

The phosphido complex $Cp'_2Nb(PPh_2)(CN\text{-2,6-}C_6H_3Me_2)$ was prepared by deprotonation of $[Cp'_2Nb(CN\text{-2,6-}C_6H_3Me_2)(PHPh_2)]Cl$ [2b] using NaOH as a base. This complex undergoes the unusual cycloaddition of methyl propynoate ($HC{\equiv}CCO_2Me$) and methyl butynoate ($MeC{\equiv}CCO_2Me$), according to Scheme 22, to give the novel



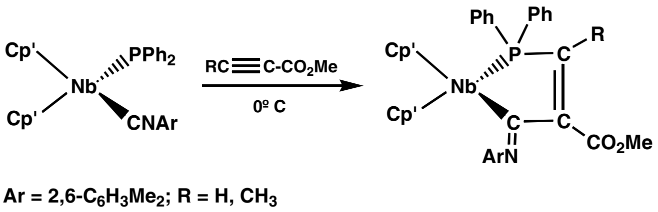
Scheme 20.



Scheme 21.

five-membered heteroniobacycles $Cp'_2Nb(\kappa\text{-}C\text{-}C(=N\text{-}2,6\text{-}C_6H_3Me_2)C(CO_2Me)=C(R)PPh_2\text{-}\kappa\text{-}P)$ (R = H, Me).

The formation of these complexes can be understood in terms of the mechanism depicted in Scheme 23. The first step involves a (1,2) insertion of the electron-deficient alkyne into the Nb–P bond to give an alkenyl-phosphine intermediate. This type of complex has been isolated in analogous reactions of electron-deficient alkynes with the complex $Cp'_2Nb(PPh_2)(CO)$ [30]. In the second step it is proposed that a new intermediate is formed by a (1,1) migratory insertion of the isocyanide ligand into the Nb–C bond, which subsequently undergoes ring closure by coordination of the phosphine group.

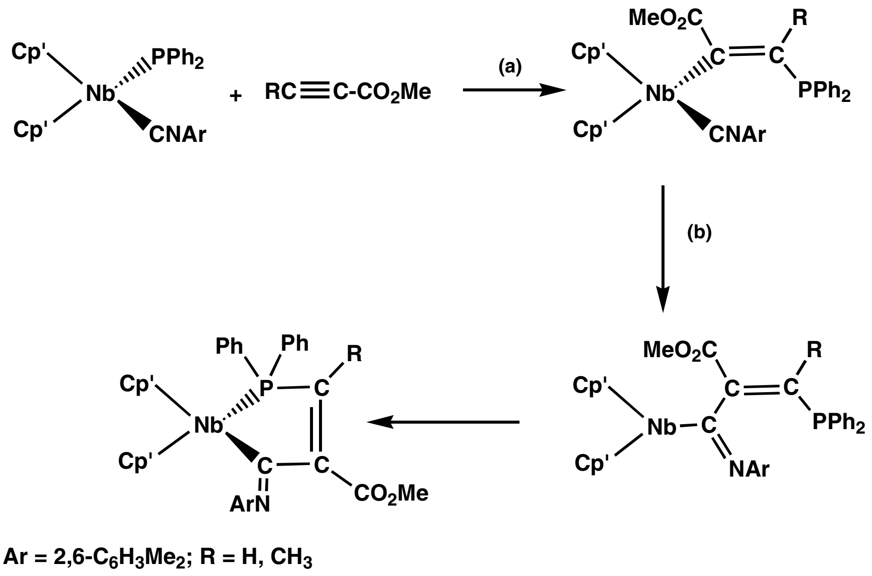


Scheme 22.

The spectroscopic data are consistent with the formation of a heteroniobacyclic moiety. The IR spectra of $Cp'_2Nb(\kappa\text{-C-C}(=N\text{-}2,6\text{-}C_6H_3Me_2)C(CO_2Me)=C(H)PPh_2\text{-}\kappa\text{-P})$ contain two bands at ca. 1617 cm^{-1} and 1585 cm^{-1} and these correspond to ν(C=N) and ν(C=C) of the iminoacyl and olefinic groups, respectively. The initially observed band for ν(C=N) in the isocyanide ligand in $Cp'_2Nb(PPh_2)(CN\text{-}2,6\text{-}C_6H_3Me_2)$ disappeared.

4. Reactivity of the Nb–P bond in niobocene derivatives

We have previously described the insertion of unsaturated molecules such as carbon monoxide and carbon dioxide, carbon disulfide, isocyanides, alkynes and alkenes into Nb–H and Nb–C bonds of niobocene complexes. As a continuation of this work, and in the field of metallophosphines, we now describe this kind of process with the Nb–P bond of phosphido complexes.



Scheme 23.

4.1. Insertion processes with CS_2

A few years ago we reported the synthesis of a new family of complexes $[Cp'_2Nb(PHPh_2)(L)]Cl$ in which L is CO or CNR [2b] and these were prepared by an insertion reaction of $ClPPh_2$ into the Nb–H bond of $Cp'_2Nb(H)(L)$. Treatment of derivatives $[Cp'_2Nb(L)(PHPh_2)]Cl$ with aqueous NaOH yielded the corresponding neutral phosphidoniobocene complexes $Cp'_2Nb(PPh_2)(L)$ by deprotonation of the P–H bond (Scheme 24). These complexes represent interesting starting materials to extend phosphorus-containing niobocene chemistry.

It is well known that dithiocarbamate ligands, $R_2NCS_2^-$, have attracted considerable attention in coordination chemistry [31], mainly due to their ability to form stable chelate complexes. However, very little effort has been directed toward investigating the analogous dialkylphosphinodithioformate ligands, $R_2PCS_2^-$. Indeed, only a few well-characterized $R_2PCS_2^-$-containing complexes of early-middle transition metals, such as Zr [32], Mo [33], and W [34], have been reported to date. Bearing this information in mind, we prepared new niobocenes containing the anionic diphenylphosphinodithioformate ligand, $R_2PCS_2^-$, namely $Cp'_2Nb(\kappa^1\text{-S-S(S)CPPh}_2)(L)$ (L = CO, CNR) and $Cp'_2Nb(\kappa^2\text{-S,S-S(S)CPPh}_2)$ [35]. The new diphenylphosphinodithioformate-containing complex $Cp'_2Nb(\kappa^1\text{-S-S(S)CPPh}_2)(CO)$ [35a] was prepared by stirring a mixture of $Cp'_2Nb(PPh_2)(CO)$ with carbon disulfide for 4 h. However, when the reaction was carried out in THF over a longer period of time, the solution became dark green and the complex $Cp'_2Nb(\kappa^2\text{-S,S-S(S)CPPh}_2)$ was isolated after the appropriate work-up (Scheme 25).

$$Cp_2'NbH_3 \xrightarrow[+\,H_2]{+\,L} Cp_2'Nb(H)(L)$$

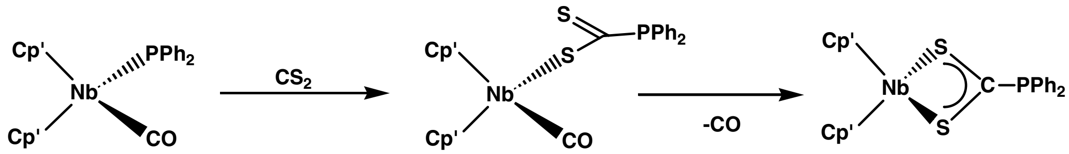
$$Cp_2'Nb(H)(L) \xrightarrow{+\,PClPh_2} [Cp_2'Nb(L)(PHPh_2)]Cl$$

$$[Cp_2'Nb(L)(PHPh_2)]Cl \xrightarrow{+\,NaOH} Cp_2'Nb(PPh_2)(L)$$

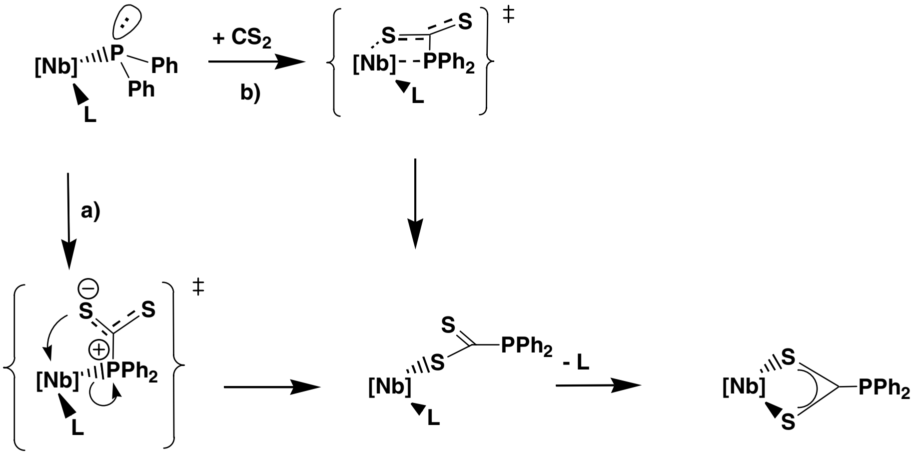
Scheme 24.

The new diphenylphosphinodithioformate-containing niobocene $Cp'_2Nb(\kappa^1\text{-S,S-S(S)CPPh}_2)(CO)$ represents the first example in which the ligand has been characterized by X-ray diffraction techniques.

The mechanism proposed for $Ph_2P(S)CS^-$ ligand formation in $Cp'_2Nb(\kappa^1\text{-S-S(S)CPPh}_2)(CO)$ is represented in Scheme 26. The formation of the $Ph_2P(S)CS^-$ ligand in an insertion reaction can be understood in terms of the interaction between the Nb–PPh_2 moiety and the heterocumulene species CS_2. Two intermediate species are possible and both of these evolve to give the complex $Cp'_2Nb(\kappa^1\text{-S-S(S)CPPh}_2)(CO)$. The first possibility (a)



Scheme 25.



[Nb] = [Nb(η^5-$C_5H_4SiMe_3$)$_2$]

L = CO, CNR

Scheme 26.

involves initial nucleophilic attack of the coordinated phosphido ligand, through the lone electron pair on the phosphorus atom, onto the electron-deficient carbon atom (electrophilic center) of CS_2 to give a zwitterionic intermediate. This intermediate evolves to $Cp'_2Nb(\kappa^1\text{-}S\text{-}S(S)CPPh_2)(CO)$ through attack of the non-coordinated sulfur atom on the niobium metal center with the simultaneous cleavage of the Nb–P bond. The second possibility (b) is consistent with a four-centered concerted transition state obtained through an intermolecular insertion process involving the Nb–P bond and one of the C=S bonds.

The formation of $Cp'_2Nb(\kappa_2\text{-}S,S\text{-}S(S)CPPh_2)$ can be envisaged as being the result of attack of the non-coordinated S atom of the κ^1-S-diphenylphosphinodithioformate ligand on the Nb atom and concurrent CO ligand elimination. The substitution of the CO ligand in this class of niobocene, i.e. $Cp'_2Nb(\kappa^1\text{-}S\text{-}S(S)CH)(CO)$ [6], is not a common reaction. In this particular case the high stability of the $Cp'_2Nb(\kappa_2\text{-}S,S\text{-}S(S)CPPh_2)$ derivative probably provides the driving force for the formation of the $Nb(\kappa^2\text{-}S,S\text{-}S(S)CPPh_2)$ moiety.

When the starting material is $Cp'_2Nb(PPh_2)(CNR)$ ($R = {}^nBu$, Cy, 2,6-$C_6H_3Me_2$) [35b], the insertion reaction of CS_2 into the Nb–P bond yielded the corresponding products in which the diphenylphosphinodithioformate ligand, $Ph_2P(S)CS^-$, is coordinated to the niobium center in a κ^1-fashion. When the reaction mixture in THF was stirred over a longer period of time, the complex again evolved to the give the final complex $Cp'_2Nb(\kappa_2\text{-}S,S\text{-}S(S)CPPh_2)$.

4.2. Insertion processes with alkynes

In Section 3.2 we described [28] an unexpected type of reactivity in phosphido niobocene complexes containing the isocyanide ancillary ligand CN-2,6-$C_6H_3Me_2$ in its reaction with electron-poor alkynes (Scheme 22). That cycloaddition process gave rise to novel five-membered heteroniobacycles. It must be noted that the first step in this process involved a (1,2) insertion of the electron-deficient alkyne into the Nb–P bond to give an alkenyl-phosphine intermediate. This type of complex has been isolated in analogous reactions between electron-deficient alkynes and the complex $Cp'_2Nb(PPh_2)(CO)$ [30]. Attempts to characterize some of the proposed intermediates by means of NMR studies were unsuccessful. However, other alternative proposals, e.g., through a concerted transition state or by initial nucleophilic attack by the phosphido group on the electron-deficient alkyne to give a charge-separated intermediate followed by an attack on the isocyanide group [29], cannot be ruled out. In this way, we succeeded in the synthesis of heterometallacyclic niobocenes from reactions between a phosphido-isocyanide derivative and electron-deficient alkynes. These results open up a new route to prepare new types of heteroniobacycles.

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