

Reactions of the 6,6-dimethylcyclohexadienyl anion with $MCl_4(PMe_3)_2$ complexes ($M = Hf, Nb$) – Isolation of complex intramolecular coupling products

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Abstract

Reactions of $NbCl_4(PMe_3)_2$ and $HfCl_4(PMe_3)_2$ with four equivalents of the 6,6-dimethylcyclohexadienyl anion lead to $Nb(6,6-dmch)[\eta^{2,4}-(dmch)_2](PMe_3)$ and $Hf(6,6-dmch)[\eta^{3,4}-(dmch)_3](PMe_3)$. Each complex has been crystallographically characterized, and found to contain one η^5 -bound 6,6-dmch ligand, with the other dmch units coupled together to yield olefin, allyl, and diene coordinations, resulting in 18 electron configurations for these compounds.

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1. Introduction

The 6,6-dmch (dmch = dimethylcyclohexadienyl) ligand has been found to exhibit properties intermediate between those of unbridged pentadienyl ligands and the cyclopentadienyl ligand [1]. As one example, due to its intermediate separation between dienyl termini, 6,6-dmch appears to generate better overlap with metal valence orbitals, rendering it a less reactive ligand, at least in reactions with alkynes [2,3], leading to more selective alkyne incorporation, which can even take place without immediate coupling to the 6,6-dmch ligand. In contrast, other pentadienyl ligands tend to undergo multiple alkyne incorporations, thus far inevitably accompanied by couplings involving the dienyl ligand, regardless of whether the dienyl ligand possesses an edge-bridge [4] or not [5]. Additionally, similar to pentadienyl, 6,6-dmch appears to have some δ -backbonding capabilities, though to a lesser extent, which has led to it having a lesser degree of pref-

erence for metals in lower oxidation states. As a result, 6,6-dmch has, like cyclopentadienyl, been found able to exist readily in higher valent metal coordination spheres, such as the recently reported $Zr(6,6-dmch)_2X_2$ [6] and $Zr(C_5H_5)(6,6-dmch)X_2$ [7] complexes ($X = Cl, Br, I$). These constitute the first general series of higher valent metal pentadienyl compounds, and it would therefore be of interest to attempt to isolate related species for other early 2nd and 3rd row transition metals. Since the above higher valent compounds were prepared from reactions of dihaloalkanes with $Zr(6,6-dmch)_2(PMe_3)_2$ and $Zr(C_5H_5)(6,6-dmch)(PMe_3)_2$ complexes, a reasonable first step would seem to be the preparation of related analogues such as $Hf(6,6-dmch)_2(PMe_3)_2$ and $Nb(6,6-dmch)_2(PMe_3)$. Given the rich chemistry already found for low valent 6,6-dmch compounds of both titanium and zirconium [4,8], their analogous hafnium and niobium species should also prove worthy of study. Herein are reported the results of our initial reactions designed to lead to such hafnium and niobium complexes, which have led in both cases to unexpected and more complicated species.

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2. Experimental

All reactions were carried out under a nitrogen atmosphere in Schlenk apparatus. THF and C₆D₆ were dried over sodium or sodium benzophenone ketyl, and distilled under a nitrogen atmosphere before use. Other solvents were passed through activated alumina columns under a nitrogen atmosphere before use. NbCl₄(THF)₂ [9], HfCl₄(THF)₂ [10], and K(6,6-dmch) [1] were prepared as previously described, or by minor variations of those methods. Elemental analyses were obtained from Desert Analytics. Proton NMR assignments for **2** were aided by the use of a COSY spectrum.

2.1. Nb(6,6-dmch)[η^{2,4}-(dmch)₂](PMe₃) (**1**)

To a yellow powder sample of NbCl₄(THF)₂ (1.62 g, 4.28 mmol) at −78 °C was added 20 mL THF. Next, PMe₃ (0.88 mL, 8.6 mmol) was added, resulting in a yellow-green mixture. K(6,6-dmch) (2.50 g, 17.1 mmol) in 30 mL THF was then added dropwise via a pressure equalizing addition funnel. The reaction mixture turned orange and was slowly warmed to room temperature, and thereafter allowed to stir for 3 h. The solvent was then removed *in vacuo* to give a dark-brown solid. Extraction of the solid with ca. 200 mL of hexanes and filtration through a Celite pad on a medium frit gave a dark orange solution. Concentration *in vacuo* of the filtrate to ca. 10 mL and cooling to −60 °C gave 0.61 g (30%) of the product.

¹H NMR (benzene-*d*₆, ambient; selected peaks): δ 2.12 (s, 3H, CH₃), 1.47 (s, 3H, CH₃), 1.17 (s, 3H, CH₃), 1.03 (s, 3H, CH₃), 0.78 (s, 3H, CH₃), 0.72 (d, 9H, *J* = 4.8 Hz, PMe₃), 0.49 (s, 3H, CH₃).

Anal. Calc. for C₂₇H₄₂PNb: C, 66.11; H, 8.63. Found: C, 66.01; H, 8.41%.

2.2. Hf(6,6-dmch)[η^{3,4}-(dmch)₃](PMe₃) (**2**)

A 1.0 g sample of HfCl₄ (3.1 mmol) was slurried in 5 mL of toluene in a 3-neck, 250 mL flask equipped with an inlet, pressure equalizing dropping funnel charged with 1.81 g of K(6,6-dmch) (12.4 mmol), and a stir bar. At room temperature, 15 mL of THF was added slowly via a syringe to the rapidly stirred slurry. The HfCl₄ rapidly reacted with evolution of heat and dissolved to give a clear solution. The flask was then cooled to −78 °C and 0.65 mL (6.2 mmol) of PMe₃ was added to give a slightly pink slurry. The K(6,6-dmch) in the addition funnel was dissolved in 20 mL of THF and was then added dropwise to the flask over 20 min to produce a red-orange solution that was allowed to warm to room temperature and stirred for an additional hour. The solvent was removed *in vacuo* and the residue was extracted with three 20 mL aliquots of pentane, followed by three 20 mL aliquots of ether. All extracts were filtered through a coarse frit covered by 1 cm of Celite and the filtrate was concentrated to ca. 5 mL *in vacuo*. Placement of the solution in a −30 °C free-

zer for several days yielded no crystalline product, but upon placing a seed crystal of Zr(dmch)₂(PMe₃)₂ into a 0 °C solution, large bright red cubic crystals of the compound began to precipitate. Placement of the flask in a −30 °C freezer overnight yielded 1.21 g (57%) of well formed cubic crystals. Analytically pure material present as small orange crystals was obtained through recrystallization of the compound from a 1:1 mixture of ether and pentane.

¹H NMR (benzene-*d*₆, ambient): δ 6.10 (d, 1H, *J* = 10.4 Hz, H18), 5.88 (bs, 1H, H20), 5.76 (d, 1H, *J* = 10.4 Hz, H17), 5.56 (m, 2H, H26,27), 5.3–5.2 (m, 2H, H3 and H29 or H30), 4.85 (td, 1H, *J* = 7.5, 2.1 Hz, H4 or H2), 4.36 (ddd, 1H, *J* = 7.9, 5.3, 1.4 Hz, H10), 4.26–4.12 (m, 2H, H11,12), 3.90 (dd, 1H, *J* = 8.4, 1.8 Hz, H2 or H4), 3.70 (dt, 1H, *J* = 7.2, 2.4 Hz, H29 or H30), 3.41 (dd, 1H, *J* = 7.9, 1.9 Hz, H9), 3.16 (s, 1H, H17), 2.97 (dt, 1H, *J* = 7.5, 2.0 Hz, H13), 2.70 (bs, 1H, H25), 2.44 (s, 1H, H1 or H5), 2.15 (s, 1H, H1 or H5), 1.61 (s, 3H, CH₃), 1.47 (s, 3H, CH₃), 1.26 (s, 3H, CH₃), 1.2 (overlap w/Me's 1H, H21), 1.18 (s, 3H, CH₃), 1.16 (s, 6H, CH₃), 0.91 (s, 3H, CH₃), 0.82 (d, 9 H, *J* = 4.9 Hz, PMe₃), 0.53 (s, 3H, CH₃).

¹³C NMR (benzene-*d*₆, ambient): δ 135.7, 135.5, 131.7, 128.1, 114.54, 114.50, 113.1, 112.2, 94.8, 89.3, 83.7, 83.3, 80.3, 79.4, 71.4, 69.3, 65.0, 56.8, 55.6, 40.2, 37.3, 36.8, 36.2, 35.7, 33.5, 32.1, 31.5, 31.0, 28.21, 28.20, 28.1, 27.1, 16.1 (d, 3C, *J* = 13.1 Hz, PMe₃).

Anal. Calc. for C₃₅H₅₃HfP: C, 61.53; H, 7.82. Found: C, 61.14; H, 7.70%.

Table 1
Crystallographic parameters for Nb(6,6-dmch)[η^{2,4}-(dmch)₂](PMe₃) (**1**) and Hf(6,6-dmch)[η^{3,4}-(dmch)₃](PMe₃) (**2**)

Formula	C ₂₇ H ₄₂ PNb	C ₃₅ H ₅₃ PHf
Formula weight	490.49	683.23
Temperature (K)	150(1)	150(1)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	14.6756(4)	10.5732(1)
<i>b</i> (Å)	10.8874(2)	12.5590(2)
<i>c</i> (Å)	15.8240(5)	12.8838(2)
α (°)	90	78.8405(9)
β (°)	100.9621(13)	74.2803(11)
γ (°)	90	72.4636(11)
Volume (Å ³)	2482.21(11)	1558.59(4)
<i>Z</i>	4	2
<i>D</i> _{calc} (Mg/m ³)	1.312	1.456
Absorption coefficient (cm ^{−1})	5.60	34.19
θ Range (°)	2.5–27.5	1.7–27.5
Limiting indices	−18 ≤ <i>h</i> ≤ 19, −13 ≤ <i>k</i> ≤ 14, −20 ≤ <i>l</i> ≤ 20	−13 ≤ <i>h</i> ≤ 13, −14 ≤ <i>k</i> ≤ 16, −16 ≤ <i>l</i> ≤ 14
Reflections collected	9844	10548
Independent reflections; <i>n</i> : [<i>I</i> > <i>nσ</i> (<i>I</i>)]	5651; 2	7045; 2
<i>R</i> (<i>F</i>)	0.0413	0.0217
<i>R</i> _w (<i>F</i> ²)	0.0683	0.0515
Maximum/minimum difference Fourier peaks (e Å ^{−3})	0.62/−0.57	1.10/−1.40

Table 2
Pertinent bonding parameters for Nb(6,6-dmch)[$\eta^{2,4}$ -(dmch)₂](PMe₃) (1)

Bond distances (Å)			
Nb–C1	2.601(3)	Nb–P	2.6107(8)
Nb–C2	2.459(3)	C1–C2	1.375(4)
Nb–C3	2.406(3)	C2–C3	1.418(4)
Nb–C4	2.419(3)	C3–C4	1.408(4)
Nb–C5	2.544(3)	C4–C5	1.380(4)
Nb–C9	2.388(3)	C9–C10	1.425(4)
Nb–C10	2.343(3)	C10–C11	1.398(4)
Nb–C11	2.386(3)	C11–C12	1.413(4)
Nb–C12	2.395(3)	C18–C19	1.432(4)
Nb–C18	2.318(3)	C19–C20	1.461(4)
Nb–C19	2.344(3)	C20–C21	1.336(4)
Bond angles (°)			
C1–C2–C3	120.8(3)	C9–C10–C11	113.8(3)
C2–C3–C4	117.1(3)	C10–C11–C12	117.4(3)
C3–C4–C5	119.5(3)		

Table 3
Pertinent bonding parameters for Hf(6,6-dmch)[$\eta^{3,4}$ -(dmch)₃](PMe₃) (2)

Bond distances (Å)			
Hf–C1	2.664(3)	Hf–C20	2.687(3)
Hf–C2	2.540(3)	Hf–P	2.7298(8)
Hf–C3	2.519(3)	C1–C2	1.383(4)
Hf–C4	2.547(3)	C2–C3	1.414(4)
Hf–C5	2.698(3)	C3–C4	1.426(4)
Hf–C9	2.438(2)	C4–C5	1.372(4)
Hf–C10	2.393(3)	C9–C10	1.421(4)
Hf–C11	2.441(2)	C10–C11	1.399(4)
Hf–C12	2.430(3)	C11–C12	1.422(4)
Hf–C18	2.480(3)	C18–C19	1.394(4)
Hf–C19	2.414(3)	C19–C20	1.396(4)
Bond angles (°)			
C1–C2–C3	121.5(3)	C9–C10–C11	113.8(2)
C2–C3–C4	115.9(3)	C10–C11–C12	117.5(2)
C3–C4–C5	120.7(3)	C18–C19–C20	121.7(2)

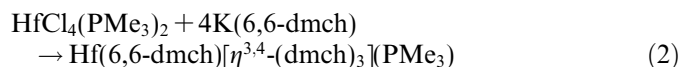
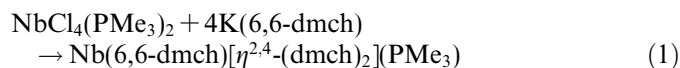
2.3. Crystallographic studies

Single crystals of each compound were selected under Paratone oil, and transferred to an Enraf-Nonius Kappa CCD diffractometer for low temperature unit cell determination and data collection. A cold nitrogen stream was used to maintain nearly constant low temperatures, and to protect the compounds from air. The niobium and hafnium structures were solved by SIR-97 and DIRDIF-99, respectively, and improved from difference Fourier maps and least-squares refinements using SHELXL-97. For both structures, all non-hydrogen atoms were refined anisotropically, while the hydrogen atoms could all be successfully refined isotropically. Pertinent crystallographic information is contained in Table 1, while selected bonding parameters are given in Tables 2 and 3.

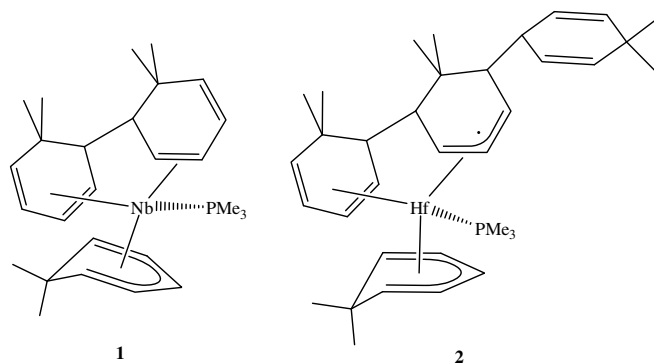
3. Results and discussion

While the MCl₄(PR₃)₂ complexes for M = zirconium, niobium, or hafnium all yield M(2,4-C₇H₁₁)₂(PR₃) prod-

ucts (C₇H₁₁ = dimethylpentadienyl; R = Me, Et) on reaction with four equivalents of the 2,4-dimethylpentadienyl anion [11], analogous reactions for the 6,6-dmch anion (dmch = dimethylcyclohexadienyl) do not proceed quite the same. For zirconium, the difference is relatively small, as one isolates 18 electron bis(phosphine) adducts such as Zr(6,6-dmch)₂(PMe₃)₂ [12], rather than 16 electron mono-adducts. However, for niobium and hafnium quite different courses are followed, leading to much more complicated products in which three or four equivalents of 6,6-dmch remain in the complexes, respectively, Eqs. (1) and (2):



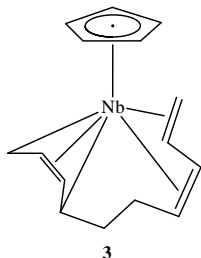
For both diamagnetic products, having stoichiometries Nb(6,6-dmch)₃(PMe₃) (1) and Hf(6,6-dmch)₄(PMe₃) (2), one uncoupled 6,6-dmch ligand is present, while the remaining two or three have undergone intramolecular coupling reactions to yield 18 electron complexes.



The formation of these products with more than two 6,6-dmch fragments can be attributed to the pronounced ability of 6,6-dmch to tolerate metals in higher oxidation states. While 2,4-C₇H₁₁ anions are more readily expelled from their complexes, and thus much more readily serve as reducing agents, multiple 6,6-dmch ligands may be retained in the coordination sphere, where they may subsequently undergo intramolecular coupling reactions. Nonetheless, the loss of one 6,6-dmch ligand from the niobium coordination sphere suggests that the first 6,6-dmch anion in that case does serve as a one electron reductant. Given the availability of the Nb(III) oxidation state, as in NbCl₃(dme) for example [13], this appears reasonable; in contrast, Hf(III) coordination complexes are less common [14].

A similar course has actually been observed in the reaction of Nb(C₅H₅)Cl₄ with four equivalents of the C₅H₇ (pentadienyl) or 2,4-C₇H₁₁ anion [15]. The isolated products contain an η^5 -C₅H₅ ligand and, like 1, two coupled pentadienyl fragments. Thus, the first two equivalents of the anion served as reducing agents, bringing the niobium

oxidation state down to +3. Due to the absence of a phosphine ligand, this complex achieves the 18 electron count from coordination by all eight, rather than six, unsaturated carbon atoms of the coupled decatetraene, leading to η^4 -*cis*-enediyl and η^4 -*trans*-diene coordinations, as in **3**.



The molecular structures of **1** and **2** have been established through X-ray diffraction studies (Figs. 1 and 2, Tables 2 and 3). The niobium complex can be seen to have simple η^5 -6,6-dmch and PMe_3 ligands ($d(\text{Nb}-\text{P}) = 2.6107(8) \text{ \AA}$), as well as a $\eta^{2,4}$ -decatetraene ligand formed via the intramolecular coupling between diene termini of two 6,6-dmch ligands. These coordinations lead to an 18 electron count for this complex. While pentadienyl couplings generally occur preferentially at the diene termini, that is not the case for the 6,6-dmch ligands, due to the steric influence of the edge-bridge [1,16]. In this case, the end–end coupling must be favored by the relative orientations of the 6,6-dmch ligands upon their initial incorporation.

An examination of the bonding parameters for **1** suggests that it may be best regarded as a Nb(III) complex, whose formal charge results from the presence of a 6,6-dmch anion, an η^4 -enediyl ligand (C9–12), and an η^2 -olefin (C18,19). The η^5 -6,6-dmch ligand coordinates to the Nb center with C3 being closest at 2.406(3) Å, with bonds to succeeding atoms (C2,4; C1,5) on either diene edge being progressively further away. This pattern, along with the short–long–long–short pattern in the C(1–5) bond distances, reflects the presence of a higher valent ($\geq +3$) metal center, whose contracted orbitals do not yield effective overlap with a relatively wide ($d(\text{C}1-\text{C}5) = 2.348 \text{ \AA}$) pentadienyl ligand. The progression in C(3), C(2,4), and C(1,5) bond distances is, however, not that pronounced, being more similar to what has been found for Ti(III) rather than Zr(IV) [17], and suggesting an oxidation state of +3 for niobium. Notably, a related Nb(III) cyclohexadienyl complex shows a reversed bonding trend, with the Nb–C3 distance being longest [18]. This could be related to the presence of π donating amide (and σ donating phosphine) ligands, which has been proposed [7,19] to provide a stabilizing influence for higher valent metal pentadienyl compounds [20].

The 1,3,7,9-decatetraene fragment, formed as a result of coupling between C13 and C17, is coordinated to niobium via six of its eight unsaturated carbon atoms. As a result of geometric constraints placed on the coordination due to

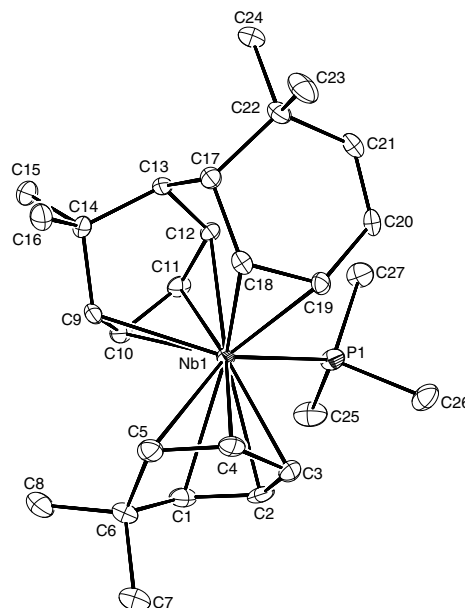


Fig. 1. Solid state structure of $\text{Nb}(6,6\text{-dmch})[\eta^{2,4}\text{-(dmch)}_2](\text{PMe}_3)$ (**1**). The 30% probability ellipsoids are shown.

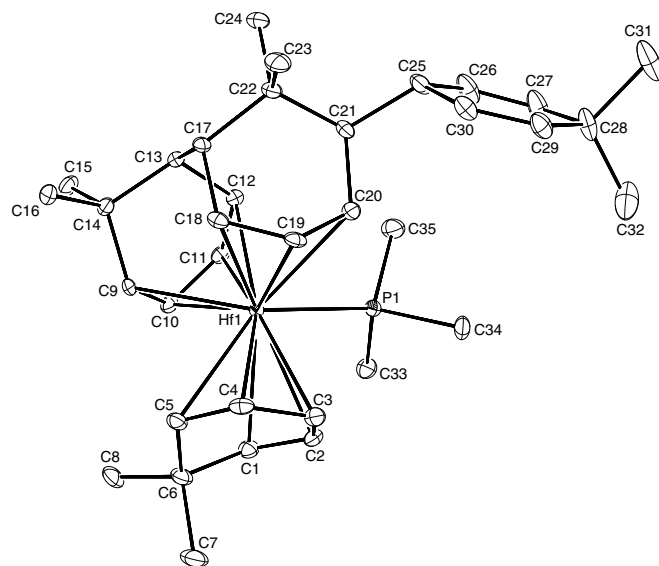
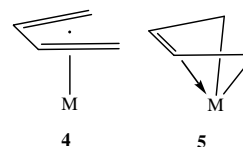


Fig. 2. Structure of $\text{Hf}(6,6\text{-dmch})[\eta^{3,4}\text{-(dmch)}_3](\text{PMe}_3)$ (**2**). The 30% probability ellipsoids are shown.

the coupling of the two 6,6-dmch units, the Nb–C bond lengths are not unambiguous in distinguishing between η^4 -diene (**4**) and η^4 -enediyl (**5**) coordination modes, though they do seem to reflect the latter more than the former, thus favoring the C(9–12) unit being formulated as a dianionic rather than neutral ligand.



The long–short–long pattern in the C(9–12) bond distances provides clearer substantiation for this assessment. The final η^2 coordination by the C18=C19 bond involves some lengthening relative to that of the uncoordinated C20=C21 bond (1.432(4) vs. 1.336(4) Å), but not so much as to justify the implication of a metallacyclopropane bonding pattern. Considering, then, C18 and C19 to be uncharged thus leads to a formal niobium oxidation state of +3, in accord with the indications from the pattern of Nb–C(1–5) bond lengths.

Complex **2** also has one η^5 -6,6-dmch ligand and a PMe_3 ligand coordinated to the metal center ($d(\text{Hf–P}) = 2.7298(8)$ Å), but additionally there are three other 6,6-dmch fragments, two of which are coupled to the third. As in **1** two of these units are coupled via diene termini (C13, C17), so that this complex may be looked upon as being related to **1** by the additional coupling of a third 6,6-dmch unit to the second diene terminus of one of the other two coupled 6,6-dmch units. Whether the formation of **2** followed a parallel path to that of **1** is not clear; conceivably one might be able to gain some mechanistic insight through attempted incorporations of fewer equivalents of ligands, which would presumably require more selective anion sources. In this regard, the location of the final 6,6-dmch fragment away from the metal center indicates that its addition involved a direct coupling as an anion rather than initial coordination to the metal. It is noteworthy that the coupling of the final 6,6-dmch unit involved its 3 position, rather than a diene terminus. The middle coupled 6,6-dmch fragment thus became an allyl ligand, best regarded as η^3 -bound, though decidedly asymmetric, with Hf–C(18–20) distances of 2.480(3), 2.414(3), and 2.687(3) Å, respectively. The similarity of the C18–C19 and C19–C20 bond lengths, 1.394(4) and 1.396(4) Å, supports the formulation of η^3 vs. η^1 -allyl coordination. The asymmetry in the allyl coordination may be due to structural difficulties in bringing all allyl and 1,3-diene carbon atoms simultaneously in bonding range of the metal center. The mono-(coupled) 6,6-dmch fragments are present as dienes, one present as a η^4 -1,3-enediyl ligand, while the 1,4-diene fragment is uncoordinated. Overall, like **1**, complex **2** also achieves an 18 electron configuration.

The carbon–carbon bond distances for the η^5 -dienyl and η^4 -enediyl ligands in **2** are quite similar to those in **1**, leading to the formulation of **2** as a Hf(IV) complex. The η^5 -dienyl coordination reflects this, with a short Hf–C3 distance (2.519(3) Å), followed by longer Hf–C(2,4) bonds (average 2.544(2) Å), and longer still Hf–C(1,5) bonds (average 2.68 Å). These are all ca. 0.11 Å longer than their Nb–C counterparts in **1**, whereas the Hf–P distance is ca. 0.12 Å longer than the Nb–P distance.

4. Conclusions

Due to the greater propensity for 6,6-dmch ligands to be retained in higher valent metal centers' coordination

spheres, routes to $\text{Hf}(6,6\text{-dmch})_2(\text{PR}_3)_n$ or related niobium species will likely have to involve either lower valent metal halide starting materials [21], or else *in situ* reduction of the higher valent metal halides with appropriate reducing agents, perhaps lithium alkyls [22]. It is also possible, however, that appropriate substitution of the diene ligands could allow for some control of the coupling processes, and lead to more desired types of products. Alternatively, for isolation of higher valent complexes such as $\text{Hf}(6,6\text{-dmch})_2\text{X}_2$ or $\text{Hf}(\text{C}_5\text{H}_5)(6,6\text{-dmch})\text{X}_2$ (X = Cl, Br, I), it may be possible to bring about the selective incorporation of 6,6-dmch ligands into appropriate Hf(IV) starting materials, perhaps through the use of less reactive formal sources of the 6,6-dmch anion. Given the rich chemistry that has thus far been observed for titanium and zirconium 6,6-dmch complexes, it can be expected that their hafnium and niobium analogues will also prove interesting, whether present in low or high oxidation states. Additionally, at least one Zr(IV) complex of the 2,4-dimethylpentadienyl ligand is known [23], and it may ultimately prove possible to expand significantly on the higher valent metal chemistry of this and other unbridged pentadienyl ligands.

Acknowledgements

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Appendix A. Supplementary material

CCDC 649541 and 649542 contain the supplementary crystallographic data for Nb and Hf. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.jorganchem.2007.06.051.

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