Higher-valent derivatives of the d-metal acids

XII. * α-Phosphonio(methylidene) complexes of niobium and tantalum containing the metallocene-like $[(\eta^5\text{-}C_5R_5)M(N^tBu)]$ core

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Abstract

The halfsandwich complexes $[(\eta^5\text{-}C_5H_5)Nb(N^tBu)Cl_2]$ (**1**) and $[(\eta^5\text{-}C_5H_5)Ta(N^tBu)Cl_2]$ (**4**) react with two equivalents of $Ph_3P{=}CH_2$ to give products of a transylidation reaction $[(\eta^5\text{-}C_5H_5)Nb(N^tBu)(CH{-}PPh_3)Cl]$ (**2**) and $[(\eta^5\text{-}C_5H_5)Ta(N^tBu)(CH{-}PPh_3)Cl]$ (**5**). The X-ray diffraction study on **2** confirms a three-legged piano stool structure. The Nb–C-distance of the α-phosphonio(methylidene) ligand is comparable with corresponding bond lengths of Schrock-type niobium alkylidene complexes. The trigonal planar $[M{=}CH{-}PR_3]$ moiety adopts a synperiplanar conformation with respect to the imido ligand, allowing both π-donor functions a minimum of competition in their interaction with empty metal d-orbitals. Treatment of **2** with an excess (4 equiv.) of $Ph_3P{=}CH_2$ leads to an equilibrium mixture of **2** and $[(\eta^5\text{-}C_5H_5)Nb(N^tBu)(CH{-}PPh_3)_2]$ (**3**). Contrastingly, by reacting lithiated ylide $Li(CH_2)_2PPh_2$ with $[(\eta^5\text{-}C_5Me_5)Ta(N^tBu)Cl_2]$ (**6**), the chelate complex $[(\eta^5\text{-}C_5Me_5)Ta(N^tBu)\{(CH_2)_2PPh_2\}Cl]$ (**7**) is isolated. **7** does not thermally rearrange to $[(\eta^5\text{-}C_5Me_5)Ta(N^tBu)(CH{-}PPh_2Me)Cl]$. However, the reaction of **7** with a second equivalent of the lithiated ylide leads to highly "π-loaded $[(\eta^5\text{-}C_5Me_5)Ta(N^tBu)(CH{-}PPh_2Me)_2]$ (**8**). The results are discussed in the context of the isolobal relationship of the fragments $[(\eta^5\text{-}C_5R'_5)M(NR)]$ (M = V, Nb, Ta), $[(\eta^5\text{-}C_5R'_5)_2M]$ (M = Ti, Zr, Hf) and $[M(NR)_2]$ (M = Cr, Mo, W).

Key words: Niobium; Tantalum; Metallocenes; Phosphorus; Ylide; Imide

1. Introduction

Phosphorus ylides $R_3P{=}CH{-}R'$ are well established reagents for C=C bond formation in organic synthesis. Contrastingly, very little is known about reactions of metal substituted phosphorus ylides $R_3P{=}CH{-}[M]$ with organic electrophiles [2]. With [M] being a strongly electron deficient complex fragment with empty d-orbitals, the bonding situation of the α-deprotonated ylide ligand is best described as α-phosphonio(methylidene) function $[M{=}CH{-}PR_3^+]$, isoelectronic with an α-silyl(alkylidene) moiety $[M{=}CR{-}SiR_3]$. Complexes of both types behave as masked carbanions exhibiting a high rotational barrier about the metal carbon double bond [3].

For *P*-methyl substituted methylenephosphoranyl complexes the number of different binding modes to the metal center increases [4]. The monoanionic ylide ligand may act as terminal, as chelating or bridging 4-electron donor (isomers **A**, **B** and **C**, **D**) (see Fig. 1).

The type of preferred coordination strongly depends on the electronical and sterical properties of the complex fragment. The chemistry of α-phosphonio(methylidene) complexes (Type **A**) has mainly focused on metallocenes of Group 4. The ylidic ligand can be introduced by either inter- or intramolecular transylidation as demonstrated by Schmidbaur and co-workers [5], Gell and Schwartz [6] and Baldwin *et al.* [7] or by an intramolecular proton shift from α-C to a π-olefin or π-arine ligand generated *in situ*. The latter method was developed by Erker and co-workers [8]. Cyclopentadienyl complexes of uranium containing the $[U{=}CH{-}PR_3]$ moiety have been described by Gilje and co-workers

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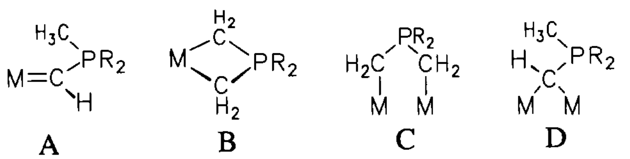


Fig. 1. Coordination modes of metallated ylides.

[9]. The trend to form an alkylidene-type of complex increases as the number of strong π-donors, *e.g.* oxo, imido or cyclopentadienyl ligands, attached to the metal center increases. Low valent and thermally rather labile α-phosphonio(carbene) complexes $[X(CO)_mM{=}CR{-}PR'_3]$ (M = Cr, Mo, W, Re) have been prepared by Fischer and co-workers by reaction of carbyne complexes with phosphanes [10].

Since it was discovered by Schrock, that activity and selectivity of well-defined olefin metathesis catalysts can be tuned by organoimido "spectator" ligands, research into synthesis and reactivity of imido(alkylidene) complexes has received particular attention [11]. Nevertheless, until recently the synthesis and reactivity of *C*-phosphonio substituted (alkylidene)imido complexes of Group 5–7 has remained an unexplored field of research. Following our studies on α-phosphonio (methylidene) complexes of chromium(VI), molybdenum(VI), tungsten(VI) and rhenium(VII) [12,13], stabilized by at least two imido ligands [14], we focused our attention on the synthesis of metal tuned ylides containing the $[(\eta^5\text{-}C_5R_5)M(N^tBu)]$ fragment (M = Nb, Ta), isolobal [15,16] with $[M(N^tBu)_2]$ (M = Cr, Mo, W) and $[(\eta^5\text{-}C_5R_5)_2M]$ (M = Ti, Zr, Hf).

2. Results and discussion

2.1. Reactions with $Ph_3P{=}CH_2$

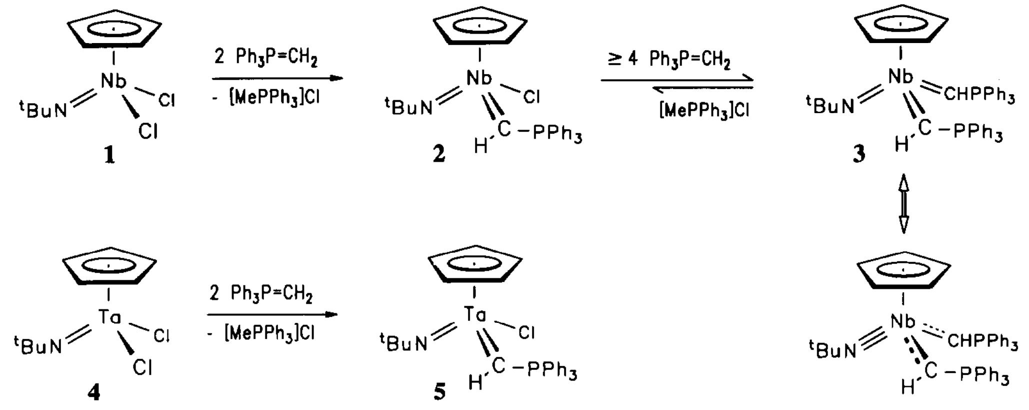
The d^0-imido complexes $[(\eta^5\text{-}C_5R_5)M(N^tBu)Cl_2]$ (M = Nb, Ta; R = H, Me) are 16-electron species exhibiting a LUMO that is mainly d_{z^2} in character and lies essentially in the MCl_2 plane. Due to the sterically less shielded metal center in comparison with electronically related metallocene dichlorides of Group 4 this acceptor orbital is accessible to small basic ligands. In accord with this postulate based on quantum-mechanical calculations, Williams *et al.* were able to structurally characterize 1:1 adducts with tertiary phosphanes [16a]. Similarly the isoelectronic d-metal (Lewis-) acids $[M(N^tBu)_2Cl_2]$ (M = Mo, W) form "classical" ylide complexes of the type $[M(N^tBu)_2(CH_2{-}PPh_3)Cl_2]$ (M = Mo, W), which are prone to elimination of HCl to give α-phosphonio(methylidene) complexes $[M(N^tBu)_2(CH{-}PPh_3)Cl]$ (M = Mo, W) in very good yield [13]. Contrastingly niobium imido complex **1** reacts with one equivalent $Ph_3P{=}CH_2$ in benzene to give a 1:1:1 mixture of starting material, $[(\eta^5\text{-}C_5H_5)Nb(N^tBu)(CH{-}PPh_3)Cl]$ (**2**) and $[Ph_3PMe]Cl$. We were not able to isolate any 1:1 ylide adduct. Obviously the rate of dehydrohalogenation of an intermediate ylide complex is faster than the initial attack of ylide at the metal center. By applying two equivalents of the ylide, **2** can be isolated in good yield. The ^1H-, ^{13}C- and ^{31}P-NMR spectra reveal the typical features of an α-phosphonio(methylidene) ligand: a characteristic downfield shift of the ^1H- and ^{13}C-resonances assigned to the α-CH moiety and a ^{31}P-shift in the region of the corresponding methyl phosphonium salt. These data together with ν(M=N–C) [17] and ν(P–C) stretching modes are listed in Table 1.

It is interesting to note that $[Cp^*TaCl_4]$ forms ylide complexes that are not deprotonated even by stronger basic *P*-methyl methylenephosphoranes [18]. The electronically related complex $[(\eta^5\text{-}C_5H_5)_2Zr(CH{-}PPh_3)Cl]$ is only formed by reaction of zirconocene dichloride with excess (> 2 equiv.) $Ph_3P{=}CH_2$ [7]. If we apply an excess (6 equiv.) of ylide, an equilibrium mixture of about 15% of **2** and 85% of the bis-sub-

TABLE 1. Selected ^1H-, ^{13}C-, ^{31}P-NMR and IR data of complexes **2**, **3**, **5**, **7**, and **8**; coupling constants in Hz (brackets), $\tilde{\nu}$ in cm^{-1} [a]

Complex		^1H	$^{13}C\{^1H\}$	$^{31}P\{^1H\}$	IR	
		M = C*H*–P (^2J(PH))	M=*C*H-P (^1J(PC))	M=CH–*P*	ν (M=N-C)	ν (P–C)
$[(\eta^5\text{-}C_5H_5)Nb(N^tBu)(CH{-}PPH_3)Cl]$	**2**	5.86 (9.1)	111.86 (33.3)	22.78	1240	920
$[(\eta^5\text{-}C_5H_5)Nb(N^tBu)(CH{-}PPh_3)_2]$	**3**	4.15 (1.8)	75.09 (n.r.)	17.04	n.m.	n.m.
$[(\eta^5\text{-}C_5H_5)Ta(N^tBu)(CH{-}PPh_3)Cl]$	**5**	5.36 (2.8)	105.12 (49.9)	27.61	1264	936
$[(\eta^5\text{-}C_5Me_5)Ta(N^tBu)(CH{-}PPh_2Me)_2]$	**8**	4.58 (1.1)	82.65 (51.8)	12.32	1240	935
$[(\eta^5\text{-}C_5Me_5)Ta(N^tBu)\{(CH_2)_2PPh_2\}Cl]$	**7**	0.09 (11.3), 0.37 (13.2)	1.27 (41.6)	19.57	1260	890
		1.15 (22.7), 1.55 (n.r.)	8.61 (42.5)			

[a] NMR spectra in C_6D_6, IR (Nujol mull); n.m. = not measured, n.r. = not resolved; for further details see experimental section.



Scheme 1. Transylidation reaction of **1** and **4** with $Ph_3P{=}CH_2$.

stituted complex $[(\eta^5\text{-}C_5H_5)Nb(N^tBu)(CH\text{-}PPh_3)_2]$ (**3**) is obtained. Obviously solubility and *CH*-acidity of the corresponding phosphonium salt $[Ph_3PMe]Cl$ in benzene is too high in order to shift the equilibrium completely to the side of product **3**. Due to similar solubility, **3** could not be isolated absolutely free of ylide and **2**, but it unambiguously was identified by its characteristic ^1H-, ^{13}C- and ^{31}P-NMR spectra. The same behaviour was observed for the reaction of the corresponding tantalum imido complex **4**. As expected, the downfield shift of the α-CH signal is slightly lower compared with the more π-acidic d^0-niobium complex **2**. A similar trend in shielding was found by Erker for a series of metallocenes $[(\eta^5\text{-}C_5H_5)_2Zr(CH\text{-}PPh_3)R]$ (M = Ti, Zr, Hf) [8c] and by us for the series of bis-imido complexes $[M(N^tBu)_2(CH\text{-}PPh_3)Cl]$ (M = Cr, Mo, W) [12,13]. Characteristic features of isoelectronic phosphonio(methylidene) complexes are compared in Table 2. If we accept chemical shifts, M–C bonding distances and rotational barriers about the M–C bond [7,8d,12,13] as a measure for the σ, π-acidity of the electronically related cationic Lewis-acids $[(\eta^5\text{-}C_5R'_5)_n\text{-}M(NR)_{2-n}]^{2+}$ (n = 0, 1, 2), we note, that despite of the formal character of oxidation states, chromium(VI) has the highest and hafnium(IV) the lowest tendency to form a highly polarized metal carbon double bond $[M{=}CH\text{-}PPh_3]$.

2.2. *Crystal structure of $[(\eta^5\text{-}C_5H_5)Nb(N^tBu)(CH\text{-}PPh_3)Cl]$ (2)*

In order to gain further insight into the bonding situation and preferred molecular conformation of **2**, single crystals were grown from n-hexane solutions and an X-ray structure analysis has been performed. The result is shown in Fig. 2. Selected bonding distances and angles are given in Table 3. Niobium possesses a slightly distorted pseudo tetrahedral geometry known as three-legged piano stool structure. The Nb–C(6) distance of 2.043(6) Å is consistent with a niobium–carbon double bond and compares perfectly with the bond length of a structurally and electronically related benzylidene imido complex $[(\eta^5\text{-}C_5Me_5)Nb(NAr)(CH\text{-}Ph)(PMe_3)]$ ($Nb\text{-}C_{bz}$ = 2.026(4) Å) recently described by Cockcroft *et al.* [16c]. The position of H(1) was found in a difference Fourier map and could be isotropically refined. The conformation of the carbanionic center C(6) is almost planar (sum of angles 359.7°). The carbon centered p-orbital perpendicular to the

TABLE 2. The effect of isolobal complex fragments [M] on selected NMR-characteristics of the $[M{=}CH\text{-}PPh_3]$ building block

Complex	Ref.	^1H, $^2J(PH)$ $M{=}CH\text{-}PPh_3$	$^{13}C\{^1H\}$, $^1J(PC)$ $M{=}CH\text{-}PPh_3$
$[Cr(N^tBu)_2(CH\text{-}PPh_3)Cl]$	[12a]	11.84 (7.6)	200.14 (35.7)
$[Mo(N^tBu)_2(CH\text{-}PPh_3)Cl]$	[13]	8.04 (0.6)	127.75 (48.8)
$[(W(N^tBu)_2(CH\text{-}PPh_3)Cl]$	[13]	6.37 (1.6)	118.19 (57.1)
$[(\eta^5\text{-}C_5H_5)Nb(N^tBu)(CH\text{-}PPh_3)Cl]$	**2**	5.86 (9.1)	111.86 (33.3)
$[(\eta^5\text{-}C_5H_5)Ta(N^tBu)(CH\text{-}PPh_3)Cl]$	**5**	5.36 (2.8)	105.12 (49.9)
$[(\eta^5\text{-}C_5H_5)_2Zr(CH\text{-}PPh_3)Cl]$	[7]	5.92 (11.1)	107.8 (31.0)
$[(\eta^5\text{-}C_5H_5)_2Hf(CH\text{-}PPh_3)Cl]$	[7]	4.37 (13.2)	97.4 (37.0)

plane defined by Nb, C(6) and P is almost coplanar (deviation 9.9°) to P–C(11) 1.820(6), which is the longest P–C_{ar} bond. By comparison with the relatively short distance C(6)–P 1.697(6) Å we have to consider an additional stabilization of the high electron density at C(6) by negative hyperconjugation [19] with the $-PPh_3^+$ substituent [20]. Structural data are consistent with resonance formulation **I** with a small contribution of **II** and **III** (see Fig. 3).

The metal–carbon double bond is short and highly polarized $M^{\delta+}-C^{\delta-}$, more than in alkylidene complexes of Schrock-type as can be depicted from ^{13}C-NMR data. Another interesting structural feature is the synperiplanar conformation of the 4-electron donor $[CH-PPh_3]^-$ with respect to the 6-electron donor $[N^tBu]^{2-}$. The dihedral angle N–Nb–C(6)–P is 5.1(2)°. A stereoelectronic preference like this is typical for oxo(alkylidene) and imido(alkylidene) complexes or in general for strong π-donor ligands in a *cis*-arrangement at a d^0-metal center [21]. This conformation allows the nitrogen ligand to form two π-bonds and the alkylidene ligand to add another π-bond to the ligand regime without using the same metal d-orbitals. As a consequence of the strong *trans*-influence of both ligands, the distances Nb–C(4) 2.508(8) and Nb–C(3) 2.497(7) Å of the C_5H_5 ring are longer than Nb–C(1) 2.401(7) Å in *cis*-position. The planar and regular ring takes off into an asymmetric position. The angle Nb–$Cp_{cent.}$–C(1) is 86.5(4)° instead of idealized 90°.

Summarizing the arguments, we should consider **2** being an 18-electron complex with a metal nitrogen triple and a polar niobium carbon double bond.

2.3. Reactions of a P-methyl substituted ylide

We are interested in generating highly "π-loaded" [22,23] imido complexes. The more π-donor ligands compete in their bonding with a given set of empty d-orbitals, the more basic and reactive in this respect will be the ligand donor atom attached to the metal. This is due to the limited number of metal π-acceptor orbitals available for ligand charge delocalization. There is a maximum of five π-bonds of different strength in case of pseudo tetrahedral complexes [24]. As the basicity of $Ph_3P{=}CH_2$ seemed to be not sufficient to shift the equilibrium towards highly π-loaded **3**, we decided to study the reaction of lithiated $MePh_2P{=}CH_2$ with $[(\eta^5\text{-}C_5Me_5)Ta(N^tBu)Cl_2]$ (**6**), the weakest d-metal acid in the series of tantalum and niobium tert-butylimido complexes described here. The 1 : 1 reaction proceeds cleanly in THF/Et_2O to give a product with two diastereotopic methylene groups arbitrarily labelled (**a**) and (**b**). By substitution of one chloro ligand a center of chirality at tantalum has been generated. The 400 MHz proton NMR shows four different non-overlapping signals corresponding to four non-equivalent protons: *endo* H_a, *exo* H_a, *endo* H_b and *exo* H_b relative to the cyclopentadienyl ring (Fig. 4). The assignment of these signals to both methylene groups is possible by comparing the geminal coupling constants ^2J(HH) in a phosphorus decoupled 400 MHz proton NMR spectrum. For each methylene group the $^1H\{^{31}P\}$ spectrum reveals a lowfield doublet of doublet next to an additional doublet at higher field. By taking into account that *endo* protons of a small rigid metallacyclic ring system attached to a halfsandwich type of

TABLE 3. Selected bond lengths (Å) and angles (°) of **2**

Bond lengths			
Nb–C(6)	2.043(6)	Nb–N	1.764(5)
Nb–Cl	2.415 (2)	Nb–$Cp_{cent.}$	2.157(7)
Nb–C(1)	2.401(7)	Nb–C(2)	2.446(7)
Nb–C(3)	2.497(7)	Nb–C(4)	2.508(8)
Nb–C(5)	2.456(7)	N–C(7)	1.452(8)
C(6)–H(1)	0.87(1)	P–C(6)	1.697(6)
P–C(11)	1.820(6)	P–C(21)	1.819(6)
P–C(31)	1.803(7)		
Bond angles			
C(1)–Nb–$Cp_{cent.}$	110.8(2)	N–Nb–$Cp_{cent.}$	121.5(2)
$Cp_{cent.}$–Nb–C(6)	111.4(3)	Nb–$Cp_{cent.}$–C(1)	86.5(4)
Nb–C(6)–H(1)	118.0(1)	P–C(6)–H(1)	111.0(2)
P–C(6)–Nb	130.7(4)	Nb–N–C(7)	164.9(4)
Cl–Nb–N	102.2(2)	Cl–Nb–C(6)	105.2(2)
N–Nb–C(6)	104.3(2)		
Dihedral angles			
N–Nb–C(6)–P	5.1(2)	Nb–C(6)–P–C(11)	80.1(2)
C(6):Σ°	359.7°		

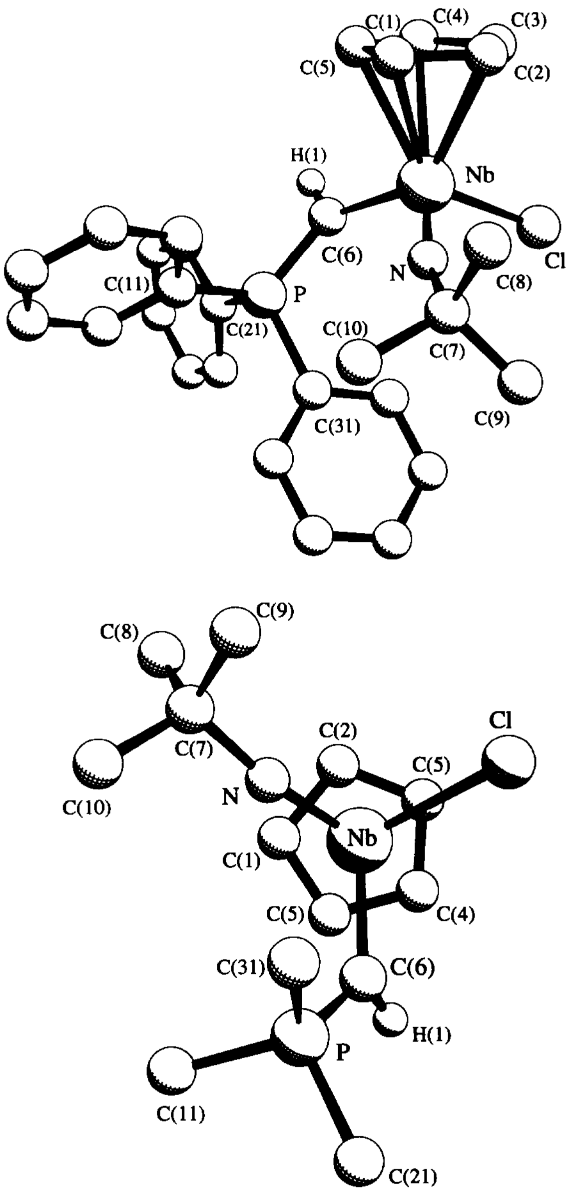


Fig. 2. Molecular structure of 2: SCHAKAL [31] projections parallel and perpendicular to the C_5H_5 ring; phenyl C-atoms beside *ipso*-C partly omitted for clarity.

fragment should appear at lower field than their *exo* counterparts [25] the signals which both show a long range ^4J(HH) coupling should be assigned to the *endo* protons. The fact that we observe an *endo–endo* but not an *exo–exo* long range coupling may be taken as indication that the metallacycle is slightly folded along the C–C axis due to steric repulsion of the *endo* phenyl group from the C_5Me_5 ring. A conformation deviating from planarity would set both *endo* C–H bonds in a syncoplanar alignment close to colinearity. The proton spectrum becomes more complicated as

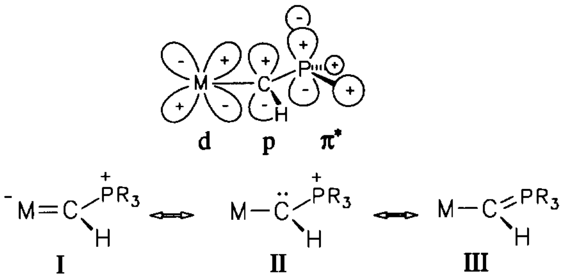


Fig. 3. Bonding situation and resonance formulae of α-phosphonio(methylidene) complexes.

coupling to the ^{31}P-nucleus is not excluded. Three different ^2J(PH) coupling constants can be registered, one signal is not resolved and appears as a multiplet. ^{13}C-NMR data is also consistent with a structure of either square pyramidal (spy) or trigonal bipyramidal (tbp) geometry. Two sets of carbon resonances for *endo* and *exo* phenyl groups can be detected.

The isolobal Lewis acid fragments $[(\eta^5\text{-}C_5R'_5)_2M]^{2+}$ (M = Ti, Zr, Hf), $[(\eta^5\text{-}C_5R'_5)M(N^tBu)]^{2+}$ (M = Nb, Ta) and $[M(N^tBu)_2]^{2+}$ (M = Cr, Mo, W) have three acceptor orbitals lying in a plane which bisects the angle $Cp_{cent.}$(or NR)–[M]–$Cp_{cent.}$(or NR) [15b,16a,25]. Therefore we prefer the *tbp* type of structure with Nb, C_a, C_b and Cl almost lying in the same plane and Cl–Ta–C_a being close to a linear axis (Fig. 4). This type of molecular geometry was confirmed by Schmidbaur *et al.* for a related zirconocene complex [5b]. It should be mentioned that most penta-coordinate molecules show distortions which lead to a solid state structure in-between the idealized *tbp* and *qpy* polyhedra.

Schwartz noted that zirconocene (**a**) (R = Me) thermally rearranges to the more stable phosphonio(methylidene) complex (**b**) [6]. The 1,3-proton shift can be either intramolecular as depicted in Scheme 2 or intermolecularly catalysed by excess ylide as suggested by Schmidbaur for the reverse type of reaction (R = NEt_2) [5].

We found that neither **7** nor the electronically related molybdenum complex (**c**) [26] rearranges to phos-

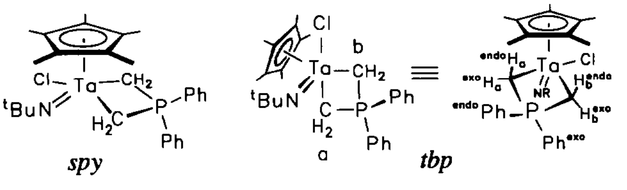


Fig. 4. Possible structures of 7.

phonio(methylidene) complexes at any spectroscopically detectable amount, when solutions in benzene were heated at 80°C for 15 hours. It seems that the chelate is thermodynamically more stable as long as sterical constraints by the ligand regime and the groups R attached to phosphorus are not compensating the chelate effect. Contrastingly to (**b**), the less crowded isoelectronic complexes **7** and (**c**) cleanly react with a second equivalent of lithiated ylide to yield tetrahedral bis-phosphonio(methylidene) complexes **8** and (**d**) [26]. In both complexes the number of ligand π-orbitals suitable for π-interaction is higher than the number of empty metal d-orbitals capable to match in π-bonding. Both complexes are highly "π-loaded". In order to obey the 18-electron rule, electron density has to remain at ligand centred non-bonding p-orbitals [27] as indicated by generally formulating M=N double bonds with a certain degree of triple bond character or M–C single bonds with a certain degree of π-bonding. In both complexes **3** and **8** the average bond order of either M=N or M=C has to be a bit lower than three or two.

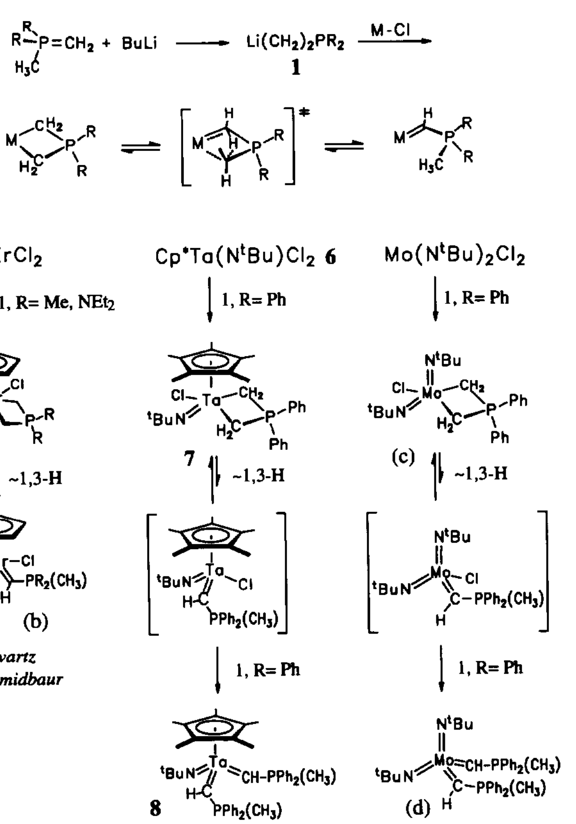
2.4. Conclusions

Similar to $[M(NR)_2Cl_2]$ (M = Cr, Mo, W) and $[(\eta^5\text{-}C_5R'_5)_2MCl_2]$ (M = Ti, Zr, Hf) the "hybrids" $[(\eta^5\text{-}C_5R'_5)M(NR)Cl_2]$ (M = Nb, Ta) behave like a "metalloyl chloride" of a d-metal acid. With ylide $Ph_3P{=}CH_2$ a rapid transylidation reaction occurs. Despite of the similarity of frontier orbitals of the metalloyl fragments, the preferred direction of fundamental reactions and equilibria may be different due to differences in steric properties (cone angles) of imido and cyclopentadienyl ligands and due to slightly different

TABLE 4. Atomic coordinates of **2** and isotropic equivalents of displacement parameters [a]

Atom	x	y	z	B_{eq} (Å^2)
NB	0.30915(4)	0.09536(3)	0.20064(3)	2.918(6)
CL	0.5733(1)	0.1484(1)	0.1363(1)	6.60(3)
P	0.1728(1)	0.25722(9)	0.38878(7)	2.86(2)
N	0.2024(4)	0.2006(3)	0.1297(2)	3.48(7)
C1	0.1495(6)	−0.0639(4)	0.1882(4)	5.3(1)
C2	0.2794(7)	−0.0719(4)	0.1130(4)	5.9(1)
C3	0.4081(6)	−0.1014(4)	0.1614(4)	6.1(1)
C4	0.3611(6)	−0.1142(4)	0.2648(4)	5.5(1)
C5	0.2018(6)	−0.0922(4)	0.2820(4)	4.9(1)
C6	0.2698(4)	0.1407(3)	0.3436(3)	3.18(8)
C7	0.1212(5)	0.2653(4)	0.0524(3)	4.4(1)
C8	0.0757(8)	0.1825(5)	−0.0148(4)	8.8(2)
C9	0.2333(8)	0.3535(5)	−0.0099(4)	8.0(2)
C10	−0.0197(8)	0.3289(6)	0.1000(5)	8.6(2)
C11	−0.0373(4)	0.2467(3)	0.4128(3)	3.18(8)
C12	−0.1091(5)	0.1780(4)	0.3578(3)	4.7(1)
C13	−0.2690(5)	0.1693(5)	0.3749(4)	6.0(1)
C14	−0.3565(5)	0.2267(5)	0.4467(4)	5.9(1)
C15	−0.2857(5)	0.2942(4)	0.5022(4)	5.1(1)
C16	−0.1269(5)	0.3044(4)	0.4856(3)	4.1(1)
C21	0.2219(4)	0.2776(4)	0.5116(3)	3.42(8)
C22	0.2725(5)	0.3825(4)	0.5301(3)	4.33(9)
C23	0.3108(6)	0.3946(4)	0.6247(3)	5.7(1)
C24	0.2995(6)	0.3019(5)	0.6984(3)	6.0(1)
C25	0.2476(6)	0.1963(5)	0.6825(3)	5.8(1)
C26	0.2091(5)	0.1843(4)	0.5874(3)	4.6(1)
C31	0.2160(5)	0.3926(3)	0.3081(3)	3.41(8)
C32	0.1101(6)	0.4854(4)	0.3027(3)	4.7(1)
C33	0.1495(7)	0.5893(4)	0.2424(4)	6.4(1)
C34	0.2954(8)	0.5995(4)	0.1873(4)	7.0(1)
C35	0.4017(7)	0.5085(4)	0.1928(4)	6.3(1)
C36	0.3635(5)	0.4052(4)	0.2520(3)	4.5(1)
H1	0.290(5)	0.089(3)	0.393(3)	2.0(9)*

[a] Starred atoms were refeined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.



Scheme 2. Transmetallation of *P*-methyl substituted phosphorus ylides at Lewis acidic and isolobal complex fragments.

energies in the HOMO/LUMO region of the complex fragments. This aspect bears fascinating perspectives for future research.

3. Experimental details

All manipulations were performed by using a high-vacuum line and standard Schlenk techniques. 4.8 Argon was dried over a column of P_4O_{10} granular. Carefully dried and oxygen-free solvents were freshly destilled before use or stored over molecular sieves for short periods. Solid organometallic compounds and ylides were stored in a argon-filled glovebox MB 150 BG-I. Melting points (uncorrected) were determined with a Büchi SMP-20 melting point apparatus or by a Thermal-Analyzer TA 9000 / duPont. NMR spectra were recorded on a Bruker AC 200 and a Bruker AMX 400 instrument. IR spectra were recorded on a Bruker IFS 25 and a Perkin-Elmer 1420 spectrometer. Mass spectra were obtained with a Finnigan MAT 90 spectrometer. Elemental analyses (C, H, N by combustion) were performed by the Microanalytical Laboratory at our department.

3.1. Preparations

$[(\eta^5\text{-}C_5H_5)Nb(N^tBu)Cl_2]$ (**1**), $[(\eta^5\text{-}C_5H_5)Ta(N^tBu)Cl_2]$ (**4**) and $[(\eta^5\text{-}C_5Me_5)Ta(N^tBu)Cl_2]$ (**6**) were prepared as described previously [28]. $Li(CH_2)_2PPh_2$ was prepared by a literature procedure [29]. The preparations of **2** and **5** can be up-scaled (< 4 g) without loss of yield.

3.1.1. *$[(\eta^5\text{-}C_5H_5)Nb(N^tBu)(CH\text{-}PPh_3)Cl]$ (2)*

A solution of 105 mg (0.35 mmol) of $(\eta^5\text{-}C_5H_5)Nb(N^tBu)Cl_2$ **1** in 7 ml of benzene was treated at 6°C with a solution of 198 mg (0.72 mmol) of $Ph_3P{=}CH_2$ in 7 ml of benzene. The reaction mixture was then warmed to room temperature, stirred for 1 h and then 1 h at 65°C. The resulting yellow suspension was evaporated to dryness and extracted with 10 ml of Et_2O. The extract was reduced to 1/10 of the volume and 5 ml of n-hexane were added. The crystallization at −30°C gave complex **2** as a yellow, crystalline solid. Yield 104 mg (55%). M.p.: 172–174°C (dec.). Found: C, 61.79; H, 5.60; N, 2.53. $C_{28}H_{30}ClNNbP$ (539.89) calc.: C, 62.29; H, 5.60; N, 2.59%. IR (Nujol): $\tilde{\nu}$ 3068 w, 3048 w $\nu(C\text{–}H_{ar})$, 1240 s $\nu(Nb{=}N\text{–}C)$, 1212 m, 1100 m, 1016 m, 920 s $\nu(P\text{–}C)$, 852 m, 792 m, 752 m $\delta(C\text{–}H_{ar})_{oop}$, 716 m, 692 m, 620 w, 592 w, 516 m, 428 m cm^{-1}. ^1H-NMR (200.1 MHz, C_6D_6): δ 0.83 (s, 9H, $NC(CH_3)_3$), 5.86 (d, $^2J(PH) = 9.1$ Hz, 1H, NbC*H*P), 6.15 (s, 5H, C_5H_5), 7.00–7.06 and 7.62–7.70 (m, 15H, $P(C_6H_5)_3$) ppm. $^{13}C\{^1H\}$-NMR (50.3 MHz, C_6D_6): δ 31.78 (s, $NC(CH_3)_3$), 65.92 (s, $NC(CH_3)_3$), 106.66 (s, C_5H_5), 111.86 (d, $^1J(PC) = 33.3$ Hz, Nb*C*HP), 128.47 (d, $^3J(PC) = 12.0$ Hz, *m*-C), 131.41 (d, $^4J(PC) = 2.8$ Hz, *p*-C), 132.52 (d, $^1J(PC) = 85.1$ Hz, *i*-C), 133.94 (d, $^2J(PC) = 9.2$ Hz, *o*-C) ppm. $^{31}P\{^1H\}$-NMR (81.0 MHz, C_6D_6): d 22.78 (s) ppm. $m/z = 539$ (M^+, 15%), 524 ($M^+\text{–}CH_3$, 5%), 482 ($M^+\text{–}C_4H_9$, 14%), 314 ($M^+\text{–}2C_6H_5\text{–}NC(CH_3)_3$, 16%), 277 ($M^+\text{–}P(C_6H_5)_3$, 61%), 275 ($M^+\text{–}2C_6H_6\text{–}NHC(CH_3)_3\text{–}Cl$, 100%), 262 ($P(C_6H_5)_3^+$, 46%), 221 ($M^+\text{–}CH_3\text{–}C_3H_5\text{–}P(C_6H_5)_3$, 20%), 183 ($M^+\text{–}CH_3 - C_5H_5\text{–}H_2CP(C_6H_5)_3$, 60%), 77 ($C_6H_5^+$, 5%), 65 ($C_5H_5^+$, 8%), 57 ($C_4H_9^+$, 4%), 41 ($C_3H_5^+$, 5%).

3.1.2. *$[(\eta^5\text{-}C_5H_5)Nb(N^tBu)(CH\text{–}PPh_3)_2]$ (3)*

A solution of 135 mg (0.45 mmol) **1** in 7 ml of benzene was treated at 6°C with a solution of 746 mg (2.70 mmol) $Ph_3P{=}CH_2$ in 7 ml of benzene. The following procedure was analogous to the synthesis of **2**. The dark red Et_2O-extract was evaporated to dryness. The waxy residue exhibited **3** (*ca.* 85% by NMR), furthermore **2** (*ca.* 15%) and some $Ph_3P{=}CH_2$. Spectroscopic data of **3**: ^1H-NMR (200.1 MHz, C_6D_6): δ 1.08 (s, 9H, $NC(CH_3)_3$), 4.15 (d, $^2J(PH) = 1.8$ Hz, 2H,

TABLE 5. Crystal structure analysis of 3

Crystallographic section	
Compound formula	$C_{28}H_{30}ClNNbP$
Molecular mass	527.87
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell constants	by refinement of 25 reflections (10° < Θ < 14°)
a(Å)	8.732(4)
b(Å)	11.579(4)
c(Å)	13.468(3)
α(°)	82.084(23)
β(°)	81.472(30)
γ(°)	87.414(35)
V(Å^3)	1333.4
Z	2
ρ(calcd)(g cm^{-2})	1.341
μ(cm^{-1})	6.057 cm^{-1}
Data collection	
Diffractometer	Enraf-Nonius CAD4
Radiation	Mo K_α (0.70930 Å), graphite monochromator, zircon filter (factor 15.41)
Crystal size (mm^3)	0.3×0.1×0.2
Data collection	$T = 298$ K, ω/θ-scan, max. $2\theta_{max.} = 48°$, 4481 relections measured, 3855 unique reflections, 3062 observed reflections $[F_o > 3\sigma(F_o)]$
Corrections	L/P correction, linear decay correction 2.8%, empirical absorption correction (Ψ-scan, min transmission 91.84%)
Structural analysis and refinement	
Solution by	direct phase determination (SHELXS-86) [30]
Method of refinement	Full-matrix LSQ, 293 parameters, unit weights (ENRAF-NONIUS SDP)
Data to parameter ratio	10.6
R values	$R = 0.03045$, $R_w = 0.06692$
Residual electron ensity	0.283 eÅ^{-3}

Heavy atoms were refined with anisotropic thermal parameters. The position of H(1) was found in a difference Fourier map and was independently and isotropically refined. All other hydrogen atoms bonded to carbon atoms were located according to ideal geometry and included in structure factor calculations, but were not refined. SCHAKAL [31] was used for illustrating the molecular structure. Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany on quoting the depository number CSD-58045, the names of the authors and the journal citation.

NbC*H*P), 5.89 (s, 5H, C_5H_5), 7.03–7.13 and 7.89–8.01 (m, 30H, $P(C_6H_5)_3$) ppm. $^{13}C\{^1H\}$-NMR (50.3 MHz, C_6D_6): δ 32.45 (s, NC(CH$_3$)$_3$), 64.48 (s, NC(CH$_3$)$_3$), 75.09 (s, NbCHP), 104.51 (s, C_5H_5), 128.02 (d, ^3J(PC) = 11.1 Hz, *m*-C), 130.15 (d, ^4J(PC) = 1.9 Hz, *p*-C), 133.72 (d, ^2J(PC) = 9.2 Hz, *o*-C), 136.32 (d, ^1J(PC) = 80.5 Hz, *i*-C) ppm. $^{31}P\{^1H\}$-NMR (81.0 MHz, C_6D_6): δ 17.04 (s) ppm.

3.1.3. $[(\eta^5\text{-}C_5H_5)Ta(N^tBu)(CH\text{-}PPh_3)Cl]$ (5)

A solution of 97 mg (0.25 mmol) **4** in 5 ml of benzene was treated at 6°C with a solution of 145 mg (0.53 mmol) $Ph_3P{=}CH_2$ in 5 ml of benzene. The reaction mixture was warmed to 25°C, stirred for 1 h and then 4 h at 60°C. The solvent was removed *in vacuo* and the residue extracted with 15 ml Et_2O. After evaporating the yellow extract to dryness 10 ml n-pentane were added. By applying ultrasound **5** precipitates as a bright yellow, microcrystalline solid. Yield 75 mg (48%). M.p.: 195–197°C. Found: C, 54.01; H, 4.80; N, 2.21. $C_{28}H_{30}ClNPTa$ (627.93) calc.: C, 53.56; H, 4.82; N, 2.23%. IR (Nujol): 3045 w $\tilde{\nu}$(C–H$_{ar}$), 1264 s ν(Ta=N–C), 1116 m, 936 s ν(P–C), 816 w, 796 w, 752 m δ(C–H$_{ar}$)$_{oop}$, 720 m, 692 m, 492 m, 460 w, 424 m cm^{-1}. ^1H-NMR (200.1 MHz, C_6D_6): δ 0.98 (s, 9H, NC(CH_3)$_3$), 5.36 (d, ^2J(PH) = 2.8 Hz, 1H, TaC*H*P), 6.23 (s, 5H, C_5H_5), 7.12–7.20 and 7.76–7.90 (m, 15H, $P(C_6H_5)_3$) ppm. $^{13}C\{^1H\}$-NMR (50.3 MHz, C_6D_6): δ 32.99 (s, NC(CH$_3$)$_3$), 64.48 (s, NC(CH$_3$)$_3$), 105.12 (d, ^1J(PC) = 49.9 Hz, TaCHP), 106.57 (s, C_5H_5), 128.36 (d, ^3J(PC) = 11.2 Hz, *m*-C), 131.23 (d, ^4J(PC) = 2.8 Hz, *p*-C), 133.61 (d, ^1J(PC) = 85.1 Hz, *i*-C), 133.95 (d, ^2J(PC) = 9.3 Hz, *o*-C) ppm. $^{31}P\{^1H\}$-NMR (81.0 MHz, C_6D_6): δ 27.61 (s) ppm.

3.1.4. $[(\eta^5\text{-}C_5Me_5)Ta(N^tBu)(CH_2)_2PPh_2Cl]$ (7)

A solution of 174 mg (0.78 mmol) $Li(CH_2)_2PPh_2$ in 8 ml THF/Et_2O (1 : 1) was added dropwise at −80°C to a solution of 344 mg (0.75 mmol) **6** in 8 ml THF/Et_2O (1 : 1). The yellow reaction mixture was warmed to room temperature and stirred for 2 h while the suspension turned pale yellow. The solvent was removed *in vacuo*, the residue extracted with 10 ml benzene and the extract reduced to 1/10 of the volume. To bring about complete precipitation of **7**, 5 ml n-hexane were added. The solution was decanted and the precipitate was dried *in vacuo*. Bright yellow solid. Yield 310 mg (65%). M.p.: 92°C. Found: C, 52.56; H, 5.97; N, 1.99. $C_{28}H_{38}ClNPTa$ (635.99) calc.: C, 52.88; H, 6.02; N, 2.20%. IR (Nujol): $\tilde{\nu}$3030 w ν(C–H$_{ar}$), 1430 m, 1340 m, 1260 s ν(Ta=N–C), 1110 m, 1100 m, 960 w, 890 m ν(P–C), 830 m, 735 m, 680 m cm^{-1}. ^1H-NMR (400.1 MHz, C_6D_6): δ 0.09 (dd, $^2J(^aH^a_{exo}H_{endo}) = 13.8$ Hz, $^2J(P^aH_{exo}) = 11.3$ Hz, 1H, $^aH_{exo}$), 0.37 (dd, $^2J(^bH^b_{exo}H_{endo}) = 13.2$ Hz, $^2J(P^bH_{exo}) = 13.2$ Hz, 1H, $^bH_{exo}$), 0.92 (s, 9H, NC(CH_3)$_3$), 1.15 (ddd, $^2J(^bH^b_{endo}H_{exo}) = 13.2$ Hz, $^2J(P^bH_{endo}) = 22.7$ Hz, $^4J(^bH^a_{endo}H_{endo}) = 5.9$ Hz, 1H, $^bH_{endo}$), 1.55 (m,

$^2J(^a\mathrm{H}^a_{endo}\mathrm{H}_{exo}) = 13.7$ Hz, $^4J(^a\mathrm{H}^b_{endo}\mathrm{H}_{endo}) = 6.0$ Hz, 1H, $^a\mathrm{H}_{endo}$), 2.03 (s, 15H, $\mathrm{C_5(C}H_3)_5$), 6.95–7.01 (m, 6H, $\mathrm{P(C_6}H_5)_3$), 7.31–7.36 (m, 2H, $\mathrm{P(C_6}H_5)_3$), 7.65–7.74 (m, 2H, $\mathrm{P(C_6}H_5)_3$) ppm. $^1\mathrm{H}\{^{31}\mathrm{P}\}$-NMR (400.1 MHz, C_6D_6): δ 0.08 (d, $^2J(^a\mathrm{H}^a_{exo}\mathrm{H}_{endo}) = 13.8$ Hz, 1H, $^a\mathrm{H}_{exo}$), 0.37 (d, $^2J(^b\mathrm{H}^b_{exo}\mathrm{H}_{endo}) = 13.2$ Hz, 1H, $^b\mathrm{H}_{exo}$), 1.16 (dd, $^2J(^b\mathrm{H}^b_{endo}\mathrm{H}_{exo}) = 13.2$ Hz, $^4J(^b\mathrm{H}^a_{endo}\mathrm{H}_{endo}) = 5.9$ Hz, 1H, $^b\mathrm{H}_{endo}$), 1.55 (dd, $^2J(^a\mathrm{H}^a_{endo}\mathrm{H}_{exo}) = 13.7$ Hz, $^4J(^a\mathrm{H}^b_{endo}\mathrm{H}_{endo}) = 6.0$ Hz, 1H, $^a\mathrm{H}_{endo}$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR (50.3 MHz, C_6D_6): δ 1.27 (d, $^1J(\mathrm{PC}) = 41.6$ Hz, $C\mathrm{H_2P}$), 8.61 (d, $^1J(\mathrm{PC}) = 42.5$ Hz, $C\mathrm{H_2P}$) 12.19 (s, $\mathrm{C_5(}C\mathrm{H_3)_5}$), 32.04 (s, $\mathrm{NC(}C\mathrm{H_3)_3}$), 65.89 (s, $\mathrm{N}C\mathrm{(CH_3)_3}$), 114.99 (s, $C_5\mathrm{(CH_3)_5}$), 128.80 (d, $^3J(\mathrm{PC}) = 10.2$ Hz, *m*-C), 128.89 (d, $^2J(\mathrm{PC}) = 6.5$ Hz, *o*-C), 128.97 (d, $^2J(\mathrm{PC}) = 7.4$ Hz, *o*-C), 130.52 (d, $^1J(\mathrm{PC}) = 83.2$ Hz, 2*i*-C), 130.80 (d, $^4J(\mathrm{PC}) = 2.8$ Hz, *p*-C), 131.45 (d, $^4J(\mathrm{PC}) = 2.8$ Hz, *p*-C), 131.71 (d, $^3J(\mathrm{PC}) = 9.2$ Hz, *m*-C) ppm. $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR (81.0 MHz, C_6D_6): δ 19.57 (s) ppm. $m/z = 635$ ($\mathrm{M^+}$, 14%), 620 ($\mathrm{M^+{-}CH_3}$, 8%), 564 ($\mathrm{M^+{-}NC(CH_3)_3}$, 14%), 442 ($\mathrm{M^+{-}C_5(CH_3)_5{-}C(CH_3)_3}$, 82%), 213 ($\mathrm{(CH_2)_2PPh_2}$, 100%), 135 ($\mathrm{C_5(CH_3)_5}$, 2%), 71 ($\mathrm{NC(CH_3)_3}$, 2%), 57 ($\mathrm{C(CH_3)_3}$, 3%).

3.1.5. $[(\eta^5\text{-}C_5Me_5)Ta(N^tBu)(CH{-}PPh_2Me)_2]$ (8)

A solution of 116 mg (0.50 mmol) $\mathrm{Li(CH_2)_2PPh_2}$ in 8 ml $\mathrm{THF/Et_2O}$ (1:1) was added dropwise at −80°C to a solution of 115 mg (0.25 mmol) **6** in 8 ml $\mathrm{THF/Et_2O}$ (1:1). The bright yellow suspension was warmed to room temperature and stirred for 2 h while the reaction mixture turned orange. The solvent was removed *in vacuo*, the residue extracted with 10 ml n-hexane and the extract reduced to 1/3 of the volume. The crystallization at −30°C/24 h gives **8** as orange-red microcrystalline solid. Yield 123 mg (60%). M.p.: 94°C. Found: C, 61.45; H, 6.47; N, 1.68. $\mathrm{C_{42}H_{52}NP_2Ta}$ (813.77) calc.: C, 61.99; H, 6.44; N, 1.72%. IR (Nujol): $\tilde{\nu}$3030 w $\nu(\mathrm{C{-}H_{ar}})$, 1430 m, 1340 w, 1240 s $\nu(\mathrm{Ta{=}N{-}C})$, 1205 w, 1098 m, 1042 m, 972 m, 935 s $\nu(\mathrm{P{-}C})$, 882 w, 735 m, 690 m $\mathrm{cm^{-1}}$. ^{1}H-NMR (200.1 MHz, C_6D_6): δ 1.25 (s, 9H, $\mathrm{NC(C_6}H_3)_3$), 2.15 (d, $^2J(\mathrm{PH}) = 12.8$ Hz, 6H, $\mathrm{PPh_2C}H_3$), 2.24 (s, 15H, $\mathrm{C_5(C}H_3)_5$), 4.58 (d, $^2J(\mathrm{PH}) = 1.1$ Hz, 2H, $\mathrm{TaC}H\mathrm{P}$), 7.00–7.12 (m, 12H, $\mathrm{P(C_6}H_5)_3$), 7.63–7.76 (m, 8H, $\mathrm{P(C_6}H_5)_3$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$-NMR (50.3 MHz, C_6D_6): δ 12.78 (s, $\mathrm{C_5(}C\mathrm{H_3)_5}$), 19.00 (d, $^1J(\mathrm{PC}) = 69.4$ Hz, $\mathrm{PPh_2}C\mathrm{H_3}$), 35.05 (s, $\mathrm{NC(}C\mathrm{H_3)_3}$), 64.31 (s, $\mathrm{N}C\mathrm{(CH_3)_3}$), 82.65 (d, $^1J(\mathrm{PC}) = 51.8$ Hz, $\mathrm{Ta}C\mathrm{HP}$), 112.82 (s, $C_5\mathrm{(CH_3)_5}$), 128.04 (d, $^3J(\mathrm{PC}) = 12.0$ Hz, *m*-C), 128.06 (d, $^3J(\mathrm{PC}) = 10.2$ Hz, *m*-C), 129.57 (d, $^4J(\mathrm{PC}) = 2.8$ Hz, *p*-C), 129.68 (d, $^4J(\mathrm{PC}) = 2.8$ Hz, *p*-C), 131.38 (d, $^2J(\mathrm{PC}) = 9.2$ Hz, *o*-C), 131.91 (d, $^2J(\mathrm{PC}) = 9.2$ Hz, *o*-C), 138.79 (d, $^1J(\mathrm{PC}) = 72.1$ Hz, *i*-C), 140.24 (d, $^1J(\mathrm{PC}) = 74.0$ Hz, *i*-C) ppm. $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR (81.0 MHz, C_6D_6): δ 12.32 (s) ppm.

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