Titanocene Pnictinidene Complexes

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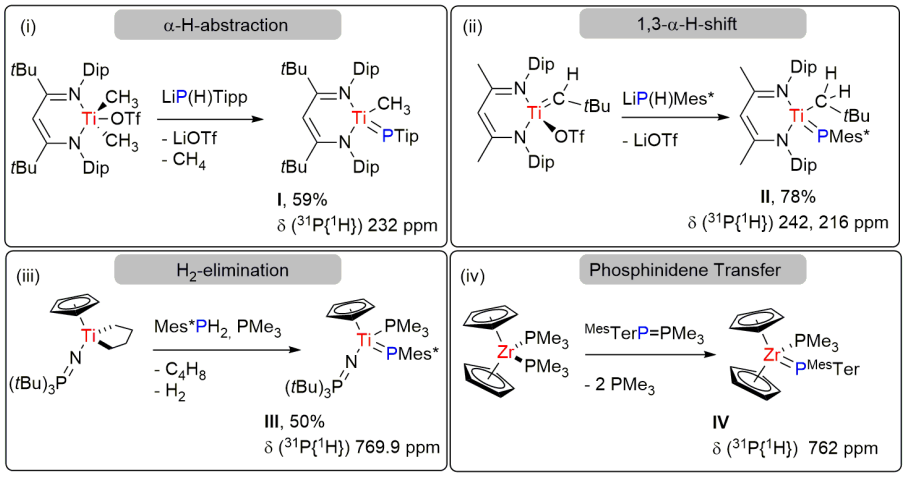
Abstract

The phospha-Wittig reagent ^{Mes}TerPPMe$_3$ (^{Mes}Ter = 2,6-{2,4,6-Me$_3$-C$_6$H$_2$}-C$_6$H$_3$) and arsa-Wittig reagent ^{Dip}TerAsPMe$_3$ (^{Dip}Ter = 2,6-{2,6-*i*Pr$_2$-C$_6$H$_3$}-C$_6$H$_3$) have been employed to synthesize the titanocene complexes Cp$_2$Ti(PMe$_3$)PnAr (Pn = P, As) with terminal phosphinidene or arsinidene ligands, respectively. *Ab initio* studies show that the description as singlet biradicaloids in their ground state is warranted.

1 Introduction

Phosphinidenes, the isovalence-electronic P-analogous of carbenes, are in contrast to the stable and widely applied *N*-heterocyclic carbenes (NHCs),[1-3] or cyclic alkyl amino carbenes (cAACs)[4, 5] mostly transient species that need to be stabilized through e.g. coordination to a transition metal fragment,[6] or by cycloaddition reactions to (conjugated) multiple bond systems as was recently shown for RP(anthracene) systems.[7] Just recently, the first example of a free kinetically stabilized phosphino-phosphinidene has been reported by Bertrand et al.[8] Together with free phosphinidenes, terminal phosphinidene complexes of the type [L$_n$M=PR] are highly desirable compounds to access a carbene-like chemistry for phosphorus-element bond

formation and phosphinidene-transfer reactions.[9-12] Nucleophilic phosphinidene complexes are preferred when the spectator ligands L are strong σ-donors, while strong π-accepting ligands render the phosphinidene unit more electrophilic.[13] In contrast to the rich chemistry of phosphinidene-bridged dinuclear complexes,[14] terminal phosphinidene complexes are rare and Mindiola et al. used sterically demanding β-diketiminate supporting ligands on titanium to access terminal phosphinidenes (Scheme 1, i and ii). Oxidation of a dimethyl complex with AgOTf and subsequent addition of LiP(H)Tip (Tip = 2,4,6-*i*Pr$_3$C$_6$H$_2$) furnished [($^{t\mathrm{Bu}}$Nacnac)(Me)Ti=PTip] (**I**, $^{t\mathrm{Bu}}$Nacnac = CH(C(*t*Bu)NDip)$_2$; Dip = 2,6-*i*Pr$_2$C$_6$H$_3$) with concomitant release of methane and LiOTf.[15] [(^{Me}Nacnac)(CH$_2$*t*Bu)Ti=PMes*] (**II**, ^{Me}Nacnac = CH(C(CH$_3$)NDip)$_2$; Mes* = 2,4,6-*t*Bu$_3$C$_6$H$_2$) was prepared from a putative neopentaylidene phosphide via a 1,3-H-shift of the α-hydrogen (Scheme 1, ii).[16] The same synthetic strategy was utilized to synthesize a Ti(IV) phosphinidene complex bearing a monoanionic PNP-pincer ligand.[17] Reaction of the Ti(II) synthon [CpTi(NP(*t*Bu)$_3$)(CH$_2$)$_4$] with Mes*PH$_2$ in the presence of PMe$_3$ afforded the corresponding base-stabilized complex [(Cp)(NP(*t*Bu)$_3$)(PMe$_3$)Ti=PMes*)] (**III**), which showed three characteristic resonances in the ^{31}P NMR spectrum at $\delta(^{31}\mathrm{P})$ = 769.9, 35.3, and −10.3 ppm for the phosphinidene, phosphinimide, and PMe$_3$ phosphorus, respectively (Scheme 1, iii).[18]

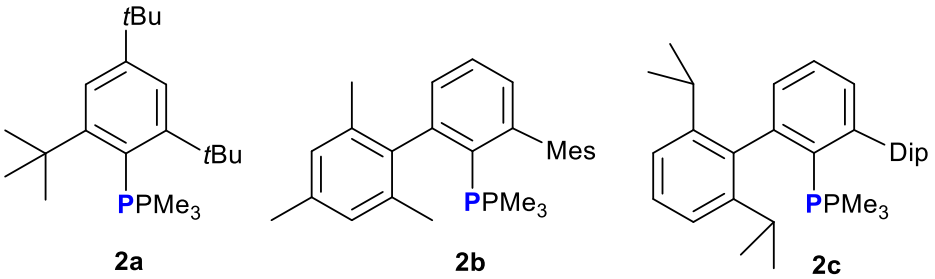


Scheme 1. Reported syntheses of selected group 4 phosphinidene complexes with the respective ^{31}P NMR shifts of the phosphinidene units.

Efficient transfer of a PAr unit can also be achieved by so-called phospha-Wittig reagents of the general type $ArP{=}PMe_3$.[19] The combination of the Zr(II) synthon $[Cp_2Zr(PMe_3)_2]$ and $^{Mes}TerPPMe_3$ (^{Mes}Ter = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$) afforded $[(Cp)_2(PMe_3)Zr{=}P^{Mes}Ter]$ (**IV**) with a characteristic deshielded phosphinidene phosphorus with a ^{31}P NMR signal at $\delta(^{31}P)$ = 762 ppm (Scheme 1, iv).[20]

Recently, we attempted the synthesis of terminal titanocene phosphinidene complexes by treatment of the Ti(II) synthon $[Cp_2Ti(btmsa)]$ (btmsa = $C_2(SiMe_3)_2$,[21] with aryl substituted triphosphiranes P_3Ar_3 (Ar = Tip, Dip, Mes), which afforded the titanocene diphosphene complexes $[Cp_2Ti(P_2Ar_2)]$ instead.[22] In this contribution we close this gap and introduce the synthesis and characterization of terminal titanocene phosphinidene and arsinindene complexes. The bonding has been thoroughly studied by combined DFT and *ab initio* studies.

As a synthetic entry we chose the titanocene precursor $[Cp_2Ti(btmsa)]$ (**1**),[23, 24] in combination with the phospha-Wittig reagents Mes*$PPMe_3$ (**2a**), $^{Mes}TerPPMe_3$ (**2b**) and $^{Dip}TerPPMe_3$ (**2c**) (Scheme 2).[25] In analogy to the synthesis of **IV** using **2b** in conjunction with $Cp_2Zr(PMe_3)_2$,[20] we first studied the formal ligand exchange reaction btmsa for PAr between **1** and **2** to give $[Cp_2Ti(PMe_3)PAr]$ *in-silico* to evaluate its thermodynamic feasibility. For all three combinations an exergonic Gibbs Free Enthalpy change to give the complexes $[Cp_2(PMe_3)Ti{=}PAr)]$ according to equation 1 ($\Delta_R G^0$ = −5.8 (**2a**), −11.2 (**2b**), −9.0 (**2c**) kcal·mol^{-1}, Eq. 1, Table S4) was obtained.[26]

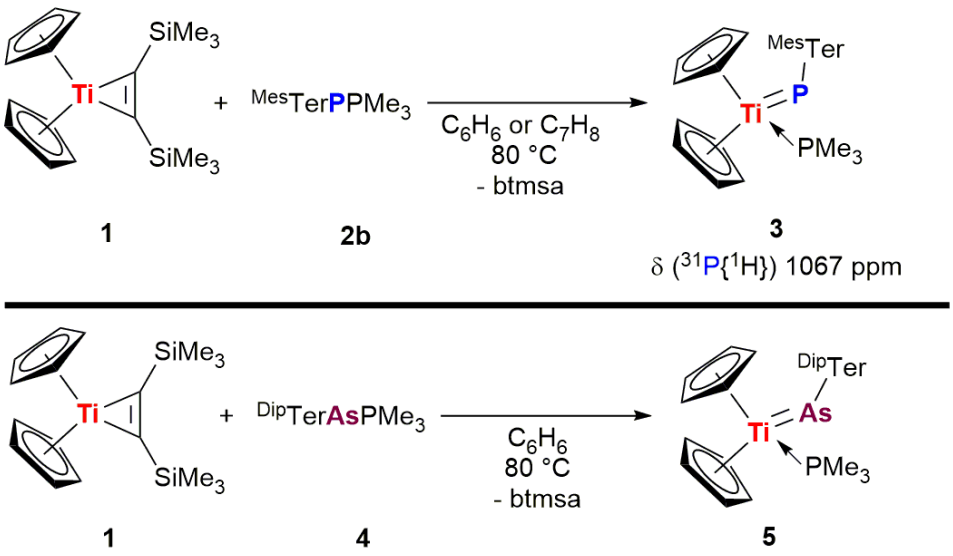


Scheme 2. Phospha-Wittig reagents **2a**-**c** utilized in this study.

(Eq. 1) $\mathrm{ArPPMe_3 + Cp_2Ti(btmsa) \rightarrow Cp_2Ti(PMe_3)(PAr) + btmsa}$

Then **1** and **2a** were combined in C_6D_6. At room temperature no reaction was observed after 16 h, but warming to 40 °C resulted in the formation of the known 3,3-dimethyl-5,7-di-*tert*-butylphosphaindane (**A**) (Figures S5-S7).[18,26,27] This suggests phosphinidene release and formal insertion of the phosphinidene unit into a C–H-bond of one *tert*-butyl methyl group, which is faster than recombination with Cp_2Ti. Phosphaindane formation is reminiscent of the reaction of the stable phosphinidene complex [$^{3t}Cp_2UPMes^*$] with diphenylacetylene, which resulted in the formation of **A** and [$^{3t}Cp_2U(C_2Ph_2)$].[28]

In contrast, treatment of **1** with **2b** on an NMR scale in C_6D_6 at 80 °C for 16 h resulted in the clean formation of a new species and complete consumption of both starting materials, accompanied by the release of btmsa ($\delta(^1H)$ = 0.15 ppm). This new compound could be unambiguously characterized to be the PMe_3 stabilized titanocene phosphinidene [$Cp_2(PMe_3)Ti{=}P^{Mes}Ter$] (**3**) by combined spectroscopic methods (Scheme 3, top). An unsymmetrical coordination environment at titanium is indicated by two signals for the Cp_2Ti unit ($\delta(^1H)$ = 5.22, 5.23 ppm) in the ^1H NMR spectrum and the signals of the terphenyl moiety are broadened, suggesting hindered rotation within the molecule. In the $^{31}P\{^1H\}$ NMR spectrum two diagnostic doublets ($^2J_{P,P}$ = 21.7 Hz) at $\delta(^{31}P\{^1H\})$ = 8.0 (PMe_3) and 1067.3 (PTer) ppm ($\delta_{calc}(^{31}P\{^1H\})$ = −41.3 (PMe_3); 1162.1 (PTer) ppm), respectively, were detected.[26] The latter being significantly deshielded by ca. 300 ppm compared to the titanium phosphinidene complex [(Cp)(NP*t*Bu)(PMe_3)Ti=PMes*)] (**III**, Scheme 1).[18] X-ray quality intensely coloured brown crystals of **3** were obtained by slowly cooling a saturated toluene solution of **3** from 80 °C to room temperature (Figure 1, left). The central titanium atom is in a trigonal-pyramidal coordination environment according to τ_4 = 0.80.[29] The Ti1–P1–C1 bond angle of 122.12(6)° is significantly more bent as in structurally characterized **I** (159.95(7)°)[6] and **II** (164.44(5)°),[15, 16] respectively. Comparable base-stabilized titanium imido complexes of the general type [$Cp_2(L)Ti{=}N^{Mes}Ter$] (L = pyridine, THF, RCN) also show Ti–N–C_{Ter} angles of over 155°.[30]



Scheme 3. Synthesis of the titanocene pnictinidene complexes **3** and **5**.

The bent geometry at the phosphorus agrees with the analogous zirconium complex [$Cp_2Zr(PMe_3)PMes^*$] (116.1(4)°).[31] The Ti1–PMe_3 bond length of 2.5688(6) Å is significantly longer than typical titanium phosphorus single bonds ($\sum r_{cov}$(Ti–P) = 2.47 Å)[32] and corresponds to dative bonding, whereas the Ti1–P1 bond length of 2.4225(6) Å is shortened but does not approach a double bond ($\sum r_{cov}$(P=P) 2.29 Å).[32] For both **I** (2.1644(7) Å) and **II** (2.1831(4) Å) significantly shorter titanium phosphorus bond lengths were found and result in pseudo-triply bonded systems.[15, 16] Attempts to synthesize a base-free titanocene phoshinidene complex using phospha-Wittig reagent **2c** with a sterically more demanding ^{Dip}Ter group did only result in decomposition of **1** at higher temperatures.[26]

The successful isolation of **3** prompted us to test whether a terminal arsinidene complex is feasible as well. To date there are two potential arsa-Wittig reagents described in the literature, $^{Tip}TerAsPMe_3$,[33] and $^{Dip}TerAsPMe_3$ (**4**).[34] Using an equimolar mixture of **4** and **1** in C_6D_6 at room temperature revealed a new signal in the ^{31}P NMR spectrum at $\delta(^{31}P)$ = 16.7 ppm after 8 h at room temperature and after heating the mixture to 80 °C over a period of 16 h full conversion of both **1** and **4** to the titanocene arsinidene complex [$Cp_2(PMe_3)Ti{=}As^{Dip}Ter$] (**5**) was detected (Scheme 3, bottom).

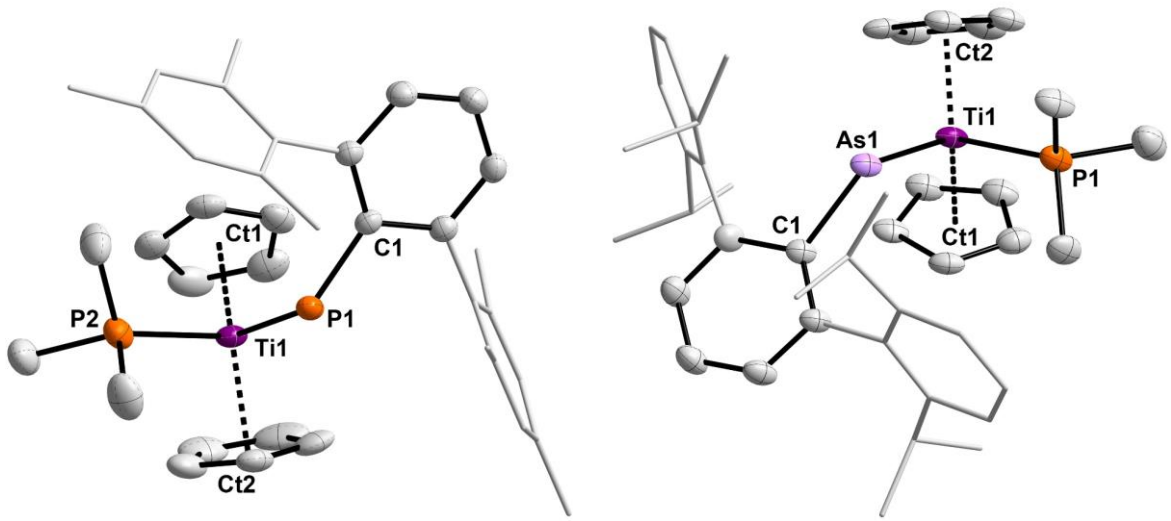


Figure 1. ORTEP drawing of the molecular structures of **3** (left) and **5** (right). Hydrogen atoms omitted for clarity and thermal ellipsoids drawn at 50% (**3**) or 30% (**5**) probability, respectively.[26]

We note that using sub-stoichiometric amounts of **1** in the reaction with **4** reproducibly gave rise to the formation of the diarsene (^{Dip}TerAs)$_2$ (**6**) as a side product. We independently showed that heating **4** to 105 °C in C_6D_6 over a period of 130 h afforded **6** quantitively based on ^{1}H NMR spectroscopy and recrystallization from *n*-pentane at −30 °C allowed the isolation of **6** in 54% yield as a yellow crystalline solid and two modifications were identified by SC-XRD experiments (Figures S3 and S4). Attempts to crystallize **5** proved difficult, however, from saturated *n*-hexane solutions X-ray quality deep brown crystals of **5** could reproducibly be grown at −30 °C. [26] **5** crystallizes in the triclinic spacegroup *P*−1 with three independent molecules in the asymmetric unit (Figure S2). As in **3**, the value of τ_4 = 0.80 is diagnostic of a trigonal-pyramidal coordination environment at titanium,[29] with a similar Ti1–As1–C1 bond angle of 121.73(10)° (cf. **3** 122.12(6)°) and corresponds to four electron donation from the arsinidene ligand to Ti (Figure 1, right). Transition metal complexes with an arsinidene ligand are rare and the herein reported **5** is the first arsinidene complex of a group 4 metal. Wolczanski et al. synthesized the first transition metal arsinidene complex (*t*BuSiO)$_3$Ta=AsPh with a Ta-As–C bond angle of 107.2(4)° and a Ta–As bond length of 2.428(2) Å ($\sum r_{cov}$(Ta=As) 2.40 Å),[32, 35] not approaching a double bond according to the

covalent radii, which is also true for **5** with a Ti1–As1 bond length of 2.4726(8) Å (Ti−As$_{avg}$ 2.4674 Å) ($\sum r_{cov}$(Ti=As) 2.31 Å, (Ti−As) 2.57 Å),[32] indicative of a weak *π*-component within this bond. It is worth mentioning that other structurally characterized arsinidene complexes were reported bearing tungsten,[36] iron,[37] and uranium metal centers.[38]

To gain a better understanding of the bonding situation in **3** and **5** we first performed an NBO analysis of the B3LYP/GD3BJ/def2tzvp optimized structures to analyse the natural localized molecular orbitals (NLMO).[26] This revealed a double bond between P1 and Ti1, in agreement with the Lewis structure in Scheme 3, however, both the π-type NBO as well as the LP at P1 are occupied by only 1.8 electrons, indicating a delocalized Ti=P double bond or a potential biradical character. Nevertheless, NLMO analysis is consistent with a Ti=P double bond, which consists of a classical sp^3-d σ-type bond (NLMO 157) and a p-d π-type bond (NLMO 158). Furthermore, the Ti−PMe$_3$ bond can be interpreted as a dative bond, with a major contribution (74%) of sp-hybrid orbitals at the P$_{PMe3}$ atom (NLMO 159). When evaluating the NLMO's of **5** (Table S12), it is immediately noticeable that these are very similar to those described beforehand for **3**. The results from NBO-analysis were corroborated by quantum theory of atoms in molecules analysis (Figure S20-21) and electron localization function (ELF) analysis (Figure S22-S23) the latter also showing a dative Ti−PMe$_3$ bond and a lone pair of electrons at the P1 (**3**) and As1 (**5**) atom, respectively.

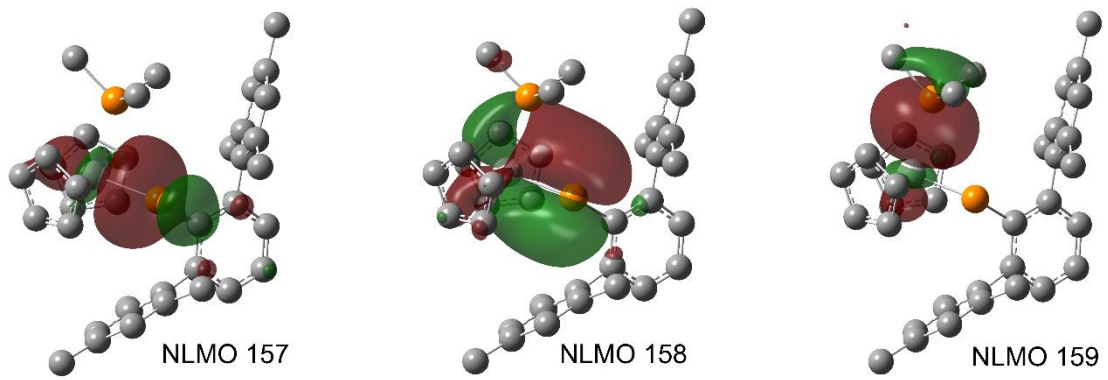


Figure 2. Representation of selected NLMOs of compound **3** (for the related NLMOs of **5** see Table S12).

Furthermore, there is a dumbbell-shaped ELF between titanium and the phosphinidene P (**3**) or arsinindene As (**5**) atom, respectively, indicating a Ti=Pn (Pn = P, As) double bond on the basis of this theory, which is further underlined by Wiberg Bind Indices of 1.73 (**3**) and 1.72 (**5**), respectively. However, both the NBO analyses and the ^{13}C-NMR high field shift of the Cp substituents of **3** (104 ppm; *c.f.* **1** δ = 118 ppm) indicate a possible delocalization of the Ti=Pn bond resulting in an electron rich titanium center.[39,40] With these results in mind, we next proofed the stability of the wave functions with respect to RHF/UHF or RKS/UKS instabilities, in order to analyse a potential biradical character of complexes **3** and **5**. While the Kohn-Sham wave function showed no instabilities, the Hartee-Fock solution exhibited a low-lying, "broken-symmetry" open-shell singlet state. Therefore, we used the Complete Active Space (CAS(2,2)) method[41, 42] to obtain a multi-determinant open-shell singlet wave function, which potentially describes the bonding situation in **3** and **5** more precisely. This calculation determined the biradical character of **3** and **5** (β(**3**) = 37%; β(**5**) =40%) to be considerable.[43] The contributions to the multi-determinant wave function are characterized by two determinants placing two electrons either in the formal HOMO (ϕ_1) or LUMO (ϕ_2) (Figure 3).

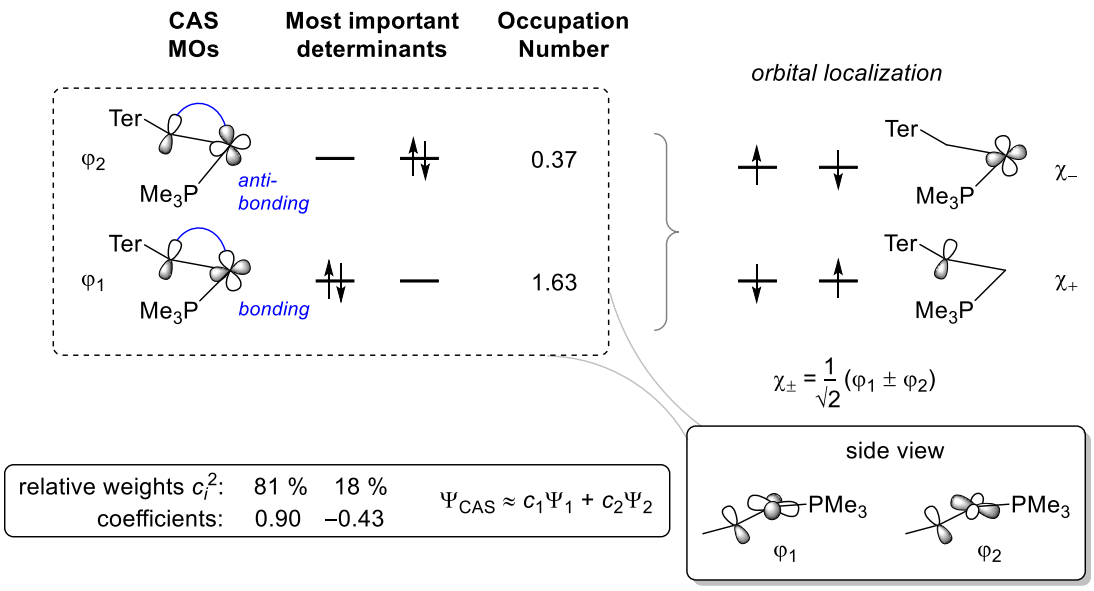


Figure 3. Schematic depiction of the active orbitals of $Cp_2Ti(PMe_3)P^{Mes}Ter$ (**3**) (CAS(2,2)/def2svpp).

The singlet state is calculated to be the ground state ($\Delta E_{S\text{-}T}$(**3**) = −106.2 KJ·mol^{-1}; $\Delta E_{S\text{-}T}$(**5**) = −96.6 KJ·mol^{-1}); i.e. the radical centres are strongly antiferromagnetically coupled. Consequently, the electronic structure can be understood as a complex between a formal Ti(III) fragment and an pnictogen-centred radical, whose "free" electrons are antiferromagnetically coupled and both complexes **3** and **5** show no indication for paramagnetically shifted NMR spectra (Figure 3, active orbitals and bonding in **3**, for **5** see Figure S25).

In summary, the syntheses of the first titanocene phosphinidene and arsinidene complexes **3** and **5** are outlined, the latter being an elusive example with a titanium arsenic double bond. These compounds became available by employing [Cp_2Ti(btmsa)] and phospha- or arsa-Wittig, respectively. Based on this study, work is currently underway on evaluating the reactivity of the herein introduced pnictogen titanium complexes.

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Conflicts of interest

There are no conflicts to declare.

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26. Experimental, computational, and details on the X-ray diffraction studies are included in the ESI. CCDC 2060154–2060157 contain the supplementary crystallographic data for this paper.

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