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COMMUNICATION

Terminal phosphinidene formation *via* tantalaziridine complexes†

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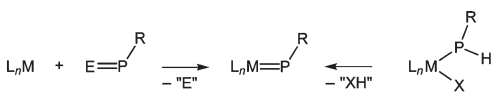
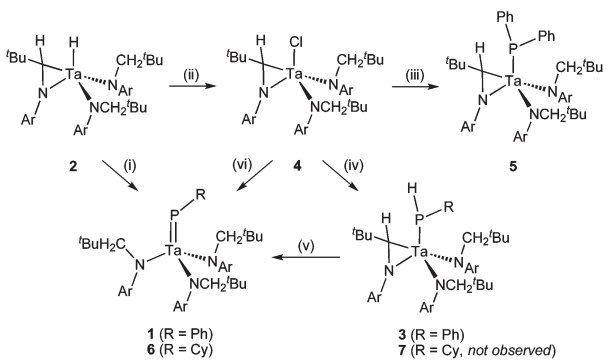
Terminal, 4-coordinate phosphinidenes of Ta supported by bulky anilide ligands are prepared by an apparent reaction sequence involving metallaziridine phosphanide complexes.

Transition metal phosphinidene complexes, *i.e.* $L_nM{=}PR$ (Scheme 1), continue to attract interest as powerful "PR" delivery reagents for synthesis.[1] Within this still relatively small class of complexes, those examples developed for transition metals in high oxidation states display nucleophilic reactivity stemming from the hard–soft metal–phosphorus bonding scenario.[2] Akin to their carbon[3] and nitrogen[4] analogs, M–P multiple bonds have been reported to engage in metathetical transformations of a range of main-group element multiple bonds.[1,2] Yet, in contrast to alkylidenes and (to a lesser extent) imides of the early transition metals, the catalytic applicability of phosphinidenes remains limited in scope.[5] With the desire to explore and develop further the M=P functionality, the pursuit of well-defined complexes featuring a terminal, nucleophilic M=P linkage represents an attractive endeavour. One synthetic approach that has captured recent attention is the installation of pre-assembled "PR" groups *via* main-group[6] or transition metal[7] based phosphinidene transfer reagents (*e.g. II* → *I*, Scheme 1). Beyond these methods, however, pathways to $L_nM{=}PR$ complexes commonly involve intermediate steps featuring proton-substituted phosphanides of the type $L_nM{-}P(H)R$;[8] ultimately, proton loss from P to furnish the M=P bond may occur *via* deprotonation,[9] elimination,[7,10] or migration[11] steps (*e.g. III* → *I*, Scheme 1).[2,12] Herein we disclose the preparation of terminal phosphinidenes by way of structural rearrangements of phosphanide complexes, a strategic variant of known methods that relies on ring-opening of three-membered Ta–C–N 'tantalaziridine' moieties.

We initially sought the anilide-supported phosphinidene, $(Ar[^tBuCH_2]N)_3Ta{=}PPh$ (**1**),[13] Scheme 2, Ar = 3,5-$Me_2C_6H_3$) *via* an analogous approach to the one that delivered the first isolable d^0 complexes that featured metal–phosphorus multiple bonds, $[(Me_3SiNCH_2CH_2)_3N]Ta{=}PR$.[14] In this effort, a salt metathesis protocol featuring the treatment of known[15] dihalide $(Ar[^tBuCH_2]N)_3TaI_2$ with two equivalents of primary phosphanide salt LiP(H)Ph indeed resulted in the production of **1**.[16] However, the targeted complex could be obtained only in low isolated yields (< 20%). A second approach involved the treatment of the previously reported tantalaziridine hydride complex $(Ar[^tBuCH_2]N)_2(\eta^2\text{-}^tBuC(H)NAr)TaH$ (**2**, Scheme 2)[15] with primary phosphine $PhPH_2$ in an effort to effect net H_2 extrusion concomitant with formation of **1**.[5a,8d,17] Again, the desired phosphinidene **1** was identified in the product mixture of this observably slow reaction, but the yield was low *in situ* and work-up was complicated by a side reaction of the H_2 byproduct with the starting hydride **2**, which produced the bridging hydride dimer $[(Ar[^tBuCH_2]N)_3Ta(\mu\text{-}H)]_2$.[16] Evidence for this competitive consumption of **2** came from its independent treatment with H_2, which led to isolation of $[(Ar[^tBuCH_2]N)_3Ta(\mu\text{-}H)]_2$ as a red-brown powder in 78% yield.[16] In an effort to improve synthetic access to **1**, we postulated that the isomeric tantalaziridine phosphanide complex **3** (Scheme 2) may provide access to the desired terminal phosphinidene *via* abstraction of the P-bound



Scheme 1 Two established routes to phosphinidenes. M = transition metal; L_n = generic ancillary ligand set; R = organic substituent; E = *e.g.*, PR_3 or L_nM'; X = *e.g.*, H, Cl, CR_3, or PR_2.



Scheme 2 Reagents: (i) for R = Ph only, 1 equiv $PhPH_2$; (ii) $CHCl_3$; (iii) $LiPPh_2$; (iv) for R = Ph only, 3 equiv LiP(H)Ph; (v) for R = Ph only, 0.5 equiv LiP(H)Ph; (vi) 1.5 equiv LiP(H)R (R = Ph, Cy).

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proton by the α-C of the three-membered metallacycle,[18] an overall process whereby the newly formed C–H bond would remain within the periphery of the supportive ligand framework.[19]

We targeted introduction of the Ta–P(H)Ph moiety in putative **3** *via* a salt metathesis reaction. In this effort, a suitable halide leaving group was installed upon the tantalaziridine platform *via* a hydride for chloride exchange reaction that involved dissolution of **2** in chloroform for 24 h. Chloride complex **4** (Scheme 2) was isolated as a yellow solid in 96% yield, and was characterized fully by standard methods including X-ray crystallography.[16] In order to provide evidence for the viability of the tantalaziridine fragment accommodating phosphanide ligands, we first targeted the secondary phosphanide **5** (Scheme 2), a complex that does not contain a P-bound proton. Complex **5** was prepared successfully by the reaction of **4** with $LiPPh_2$, and was isolated as an orange solid in 84% yield. A single resonance in the ^{31}P NMR spectrum at +112.0 ppm was attributed to the P center in **5**. Interatomic distances and angles associated with the tantalaziridine portion of **5** derived from a crystallographically determined structure (Fig. 1) were consistent with metrics for related complexes.[15] As compared to a previously reported complex featuring a terminal Ta–PPh_2 linkage, $Cp_2(H)_2TaPPh_2$,[20] the Ta–P bond length of 2.5312(6) Å found for **5** is somewhat shorter (*cf.* 2.595(3) Å), with both complexes containing approximately pyramidal phosphorus centers ($\sum\angle$ at $P \approx 319°$ for **5**, *cf.* $\approx 324°$ for $Cp_2(H)_2TaPPh_2$).

The successful production of **5** prompted us to determine if the primary phosphanide **3** was isolable *via* an analogous approach, in this case using LiP(H)Ph in place of $LiPPh_2$. We found that treatments of **4** with one equivalent of LiP(H)Ph under an assortment of reaction conditions generally led to the conversion of the chloride starting material to mixtures containing only **3** and the eventual target phosphinidene **1** in varying proportions. We were then encouraged to identify conditions whereby each complex could be isolated separately in crystalline form. In this regard, we found that the production of **3** *in situ* could be optimized when **4** was treated with excess LiP(H)Ph (3 equiv) in benzene, followed by work-up of the reaction mixture after 1 h. Under these conditions, the complete consumption of **4** was observed, and isomers **3** and **1** were determined to be present in a *ca.* 15 : 1 ratio by ^{31}P and ^{1}H NMR spectroscopy. We found that **3** could be isolated cleanly in 46% yield as yellow-orange crystals from such a mixture in Et_2O at −35 °C. An X-ray crystallographic study affirmed the expected connectivity for **3** (Fig. 1). The metrical parameters for the two independent molecules found in the asymmetric unit for **3** are comparable to those associated with the diphenyl analog **5**, with Ta–P bond lengths of 2.5543(12) and 2.5645(11) Å and Ta–P–C angles of 111.94(14) and 111.59(12)°. Although the hydrogen atom connected to P in **3** could not be definitively located in the X-ray diffraction experiment, diagnostic NMR spectroscopic features for the P–H moiety in **3** were identified by a doublet observed at −19.1 ppm ($^{1}J_{PH}$ = 229 Hz) in the ^{31}P NMR spectrum, along with a corresponding doublet at 5.39 ppm in the ^{1}H NMR spectrum with H–P coupling of the same magnitude. Regarding the stability of **3** in solution, we have observed only very gradual conversion of **3** to **1** when a crystalline sample of **3** was dissolved in C_6D_6 (*ca.* 5% after 3 d at 20 °C). Furthermore, heating of the reaction mixture at 65 °C for 2 d had minimal effect on its composition. However, we have found that addition of LiP(H)Ph in substoichiometric quantities (0.5 equiv) accelerates the conversion of **3** to **1** in a near quantitative process within 24 h, as monitored by ^{1}H and ^{31}P NMR spectroscopy.[16] It appears as though LiP(H)Ph serves as a base catalyst in the net repositioning of the P-bound proton to the alkyl group derived from the aziridine fragment in **3**.[21] Phosphinidene **1** appears to be the thermodynamically favored isomer, as the presence of **3** has not been detected spectroscopically in C_6D_6 solutions of **1** over extended time periods (14 d).

With this knowledge, a direct preparation of **1** was carried out *via* the treatment of chloride **4** with LiP(H)Ph (1.5 equiv), followed by isolation after 24 h of a spectroscopically pure deep red solid in 81% yield. A characteristic low field signal

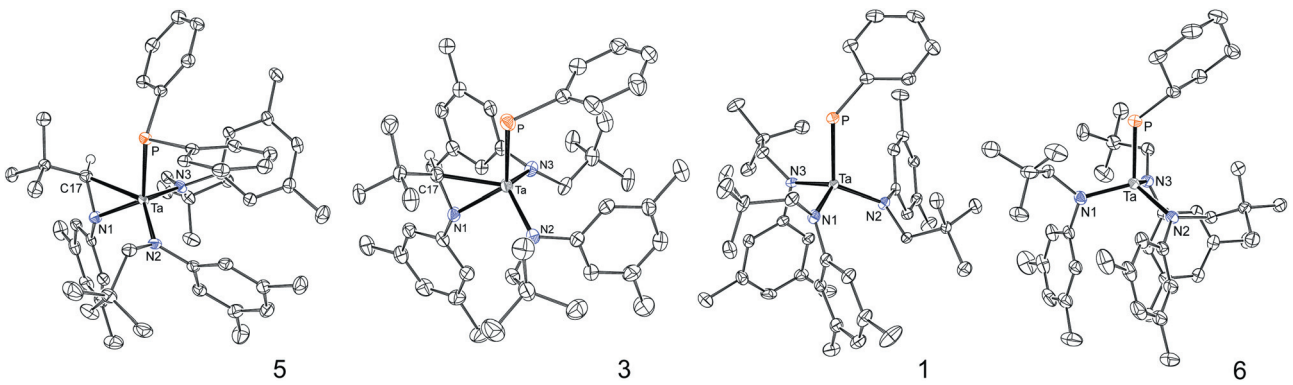

Fig. 1 Thermal ellipsoid plots of **5**, **3**, **1**, and **6** drawn at 50% probability with selected H atoms omitted for clarity. Selected interatomic distances (Å) and angles (°): **5**: Ta–P 2.5312(6), Ta–C17 2.200(2), Ta–N1 1.976(2), Ta–N2 1.9914(19), Ta–N3 1.9656(19), N1–C17 1.418(3), N1–Ta–C17 39.25(8), C17–N1–Ta 78.94(13), Ta–P–C 104.45(7) and 112.01(7), $\sum\angle$ at P ≈ 319; **3** (two independent molecules in asymmetric unit): Ta–P 2.5543(12) & 2.5645(11), Ta–C17 2.222(4) & 2.217(4), Ta–N1 1.966(3) & 1.967(3), Ta–N2 1.970(3) & 1.972(3), Ta–N3 1.966(3) & 1.967(3), N1–C17 1.427(5) & 1.420(5), N1–Ta–C17 39.25(13) & 39.10(13), C17–N1–Ta 80.1(2) & 80.0(2), Ta–P–C 111.94(14) & 111.59(12); **1**: Ta–P 2.3052(11), Ta–N1 1.989(3), Ta–N2 1.989(3), Ta–N3 2.005(3), Ta–P–C 125.15(13); **6**: Ta–P 2.2888(8), Ta–N1 1.994(2), Ta–N2 1.979(2), Ta–N3 2.021(2), Ta–P–C 130.07(10).

associated with the P center in **1** was detected at 451.6 ppm in the ^{31}P NMR spectrum, and effective C_3-symmetry in C_6D_6 solution was evident through equivalent anilide residues by ^{1}H and ^{13}C NMR spectroscopy.[16] X-ray crystallography supported the structural formulation for **1** (Fig. 1); expectedly, the Ta–P bond length of 2.3052(11) Å is significantly shorter than the respective distances in **5** and **3**, and is similar to the distance of 2.317(4) Å disclosed for the related four-coordinate phosphinidene (^{t}Bu$_3$SiO)$_3$Ta=PPh.[17a] While the Ta–P–C "bend" angle of 125.15(13)° is slightly more obtuse than that found for (^{t}Bu$_3$SiO)$_3$Ta=PPh (110.2(4)°), it is in line with structurally related trimethylsilyl- and stannyl-phosphinidenes of niobium.[8c,22]

To demonstrate generality of this approach to phosphinidenes, we targeted the cyclohexyl variant, **6** (Scheme 2). In this case, the treatment of **4** with 1.5 equivalents of LiP(H)Cy in benzene led to the isolation of **6** as a brown-red solid in 86% yield after 18 h. However, the supposed intermediate in this transformation, phosphanide complex **7** (Scheme 2), was not observed when the reaction mixture was followed by ^{1}H and ^{31}P NMR spectroscopy (in C_6D_6). In attempts to spectroscopically identify **7**, including reactions conducted at low temperatures, only the starting materials and the phosphinidene product **6** were detected *in situ*. While an alternative sequence cannot be ruled out, we postulate an analogous reaction to that which led to **3** (and ultimately **1**) takes place, but in this case intermediate **7** undergoes rearrangement to the respective terminal phosphinidene much more rapidly than phenyl counterpart **3**. Characterization data obtained for **6** revealed similar features to those found for **1**. Notably, a ^{31}P NMR resonance at 483.1 ppm was assigned to the P center in **6**. The crystallographically determined structure for **6** (Fig. 1) showed a similar Ta–P bond length of 2.2888(8) Å and a slightly less bent Ta–P–C angle (130.07(10)°) than that observed for **1**, a metric that likely arises from the increased steric demands of the cyclohexyl substituent. Each phosphinidene crystal structure **2** and **6** reveals a rotated orientation of one of the three anilide ligands perpendicular to the Ta–P vector, which is likely a geometric consequence of maximizing π-electron donation to the electrophilic Ta center.[22]

Given the precedent of related early transition-metal complexes to engage in "PR" group transfer reactions,[1,2,10] we anticipated that the four-coordinate Ta phosphinidenes **2** and **6** would function as phospha-Wittig reagents. Consistent with this regard, the separate treatments of **2** and **6** with pivaldehyde (O=C(H)^{t}Bu) effected the production of the respective phosphaalkenes, RP=C(H)^{t}Bu (R = Ph for **2**, R = Cy for **6**) in reactions that were quantitative with respect to the conversion of the aldehyde *in situ*, as assayed by NMR spectroscopy.[16]

In summary, we have reported herein the preparation of terminal phosphinidenes **2** and **6** *via* apparent reaction sequences involving the repositioning of a P-bound proton of tantalaziridine phosphanide complexes (*i.e.* **3** and putative **7**). We ascribe at least some of the favorability of this base-promoted isomerization to a confluence of ring-strain alleviation and basicity of the alkyl fragment of the tantalaziridine functional group.[18] Given the considerable interest in phosphorus-element bond formation reactions,[1,2] we aim to explore further the reactivity of these complexes beyond our preliminary experiments with pivaldehyde. Also, it remains to be seen if this strategy can be extended to produce other Ta-element multiple bonds *via* the installation of main-group fragments atop the tantalaziridine platform used herein, such as alkyl,[23] silyl, or amido groups, each equipped with a removable α-proton.

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