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On the Mechanism and Scope of Phosphinidene Transfer from Dibenzo-7-Phosphanorbornadiene Compounds

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Abstract. Dibenzo-7-phosphanorbornadiene compounds, RPA ($\mathbf{A} = \text{C}_{14}\text{H}_{10}$ or anthracene), are investigated as phosphinidene sources upon thermally induced (70–90 °C) anthracene elimination. Analysis of substituent effects reveals that π -donating dialkylamide groups are paramount to successful phosphinidene transfer; poorer π -donors give reduced or no transfer. Substituent steric bulk is also implicated in successful transfer. Molecular beam mass spectrometry (MBMS) studies of each derivative reveal dialkylamide derivatives to be promising precursors for further gas-phase spectroscopic studies of phosphinidenes; in particular, we present evidence of direct detection of the dimethylamide derivative, $[\text{Me}_2\text{N}=\text{P}]$. Kinetic investigations of $^i\text{Pr}_2\text{NPA}$ thermolysis in 1,3-cyclohexadiene and/or benzene- d_6 are consistent with a model of unimolecular fragmentation to yield free phosphinidene [$^i\text{Pr}_2\text{N}=\text{P}$] as a transient reactive intermediate. This conclusion is probed by density functional theory (DFT) calculations, which favored a mechanistic model featuring free singlet aminophosphinidenes. The breadth of phosphinidene acceptors is expanded to unsaturated substrates beyond 1,3-dienes to include olefins and alkynes; this provides a new synthetic route to valuable amino-substituted phosphiranes and phosphirenes, respectively. Stereoselective phosphinidene transfer to olefins is consistent with singlet phosphinidene reactivity by analogy with the Skell hypothesis for singlet carbene addition to olefins.

Introduction

The most thoroughly studied class of phosphinidene transfer reactions involves phosphinidene units stabilized by metal-carbonyl complexation,¹ but the chemistry of “naked” phosphinidenes is far less developed. Recent reports of new production methods for singlet phosphinidenes lacking supportive phosphorus–metal bonds, including an isolatable phosphinophosphinidene, have been enabled by strong multiple bonding between the phosphorus center and its substituent.^{2–4} This flurry of activity has allowed our understanding of these species’ reactivities and bonding patterns to rapidly unfold. We are now closer than ever to using free singlet phosphinidenes as valuable building blocks for further organophosphorus chemistry, or as varied ligands akin to *N*-heterocyclic carbenes (NHCs) in transition metal complexes.

Historically, the highly reactive nature of phosphinidenes has oftentimes required their generation under conditions excessively harsh for practical synthetic applications. The most commonly employed methods were thermolysis⁵ or photolysis⁶ of precursors such as diphosphenes,⁷ cyclic oligophosphanes,⁸ *P*-arylophosphiranes,⁹ *P*-aryl-3-phospholenes,¹⁰ or phospho-Wittig reagents.¹¹ The intermediacy of free phosphinidenes was seldom easy to prove, and their behavior was typified by triplet reactivity patterns.¹² The advent of sin-

glet phosphinophosphinidene $^t\text{Bu}_2\text{PP}$, generated from thermal phospho-Wittig fragmentation¹³ marked a major advance in the field. This phosphinidene could be delivered to reaction partners at mild temperatures, allowing elucidation of reactivity without the controversies¹⁴ sometimes caused by competing high temperature pathways.

As a new entryway to phosphinidenes, our recently reported dibenzo-7-phosphanorbornadiene RPA ($\mathbf{A} = \text{C}_{14}\text{H}_{10}$ or anthracene) compounds have shown initial promise in the transfer of phosphinidenes and related species for further reaction chemistry.^{2,15} Notable as the first isolable examples of molecules containing a P-lone pair unprotected 7-phosphanorbornadiene framework,¹⁶ these RPA compounds are attractive phosphinidene sources due to their facile preparation from commercially available dichlorophosphines RPCl_2 and $\text{MgA}\cdot 3\text{THF}$, their propensity to undergo thermal fragmentation under mild conditions, and their release of a relatively inert, crystalline, and neutral byproduct: anthracene.¹⁷

With this work, we expand our studies beyond the initial report of phosphinidene transfer from $^i\text{Pr}_2\text{NPA}$ to 1,3-cyclohexadiene (Scheme 1, $\text{R} = \text{N}^i\text{Pr}_2$).² In particular, the present study was conducted to address outstanding questions concerning the mechanism and scope of phosphinidene transfer from RPA compounds. Accordingly, we report herein a series of synthetic and kinetic investigations to probe conditions under which the intermediacy of free singlet phosphinidenes can be expected. Our experimental results are consistent with thermal phosphinidene transfer from dialkylamide-substituted R_2NPA compounds involving dissociative singlet $[\text{R}_2\text{NP}]$ production and they are also in accord

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with conclusions arising from potential energy surface explorations by way of density functional theory (DFT) quantum chemical calculations.

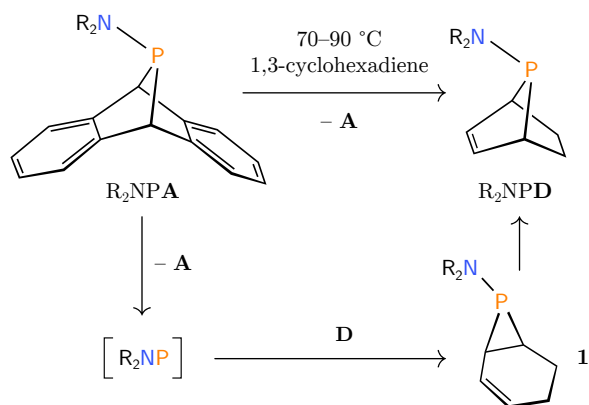
Results and Discussion

Substituent Investigations. Investigations into these phosphinidene precursors began with an expansion of our repertoire of RPA species. Through systematic substituent modification,¹⁸ we hoped to uncover factors important to phosphinidene liberation from anthracene. In this way, the scope of substituents amenable to successful phosphinidene transfer to reaction partners might be identified.

The reaction of dichlorophosphines with MgA·3THF at -78 °C in THF proved productive with a wide variety of substituents. Dialkylamide-substituted RPA compounds were generally the easiest to prepare; in addition to the species already described,^{2,19} we have found that diethylamide, dicyclohexylamide, and *cis*-2,6-dimethylpiperidide derivatives can be accessed in synthetically useful isolated yields, providing Et₂NPA (61%), Cy₂NPA (32%), and Me₂PipPA (62%), respectively. Amides of excessive steric bulk were found to preclude P–C bond formation, as 2,2,6,6-tetramethylpiperidide-substituted RPA could not be accessed from the dichlorophosphine and MgA·3THF, this reaction instead yielding only oligomeric products (RP)_{3,4}.²⁰ Mixed results were obtained with substituents less π -donating than amides. Both ^tBuPCl₂ and EtOPCl₂ reacted productively with MgA·3THF, though in diminished yield, to give ^tBuPA (20%)² and EtOPA (23%), respectively. In contrast, PCl₃ and PhPCl₂ produced neither ClPA nor PhPA upon treatment with MgA·3THF, instead giving unidentified phosphorus-containing products or cyclic oligophosphanes (PhP)_n, respectively.² In these two cases, MgA·3THF likely functioned as an outer-sphere two-electron reductant instead of the desired “double-Grignard” mode of nucleophilic C–P bond-forming reactivity.²¹

The parent derivative H₂NPA could not be accessed directly from MgA·3THF and a dichlorophosphine due to the unavailability of H₂NPCl₂. Instead, ClPA, produced from Me₂NPA and ethereal hydrogen chloride,¹⁹ was found to react with excess ammonia in dioxane solution to yield H₂NPA in 55% yield. Although aminophosphines are prone to self condensation,²² the identity of this product was confirmed to be H₂NPA rather than HN(PA)₂ by solution NMR spectroscopy and an X-ray diffraction study (SI §S.5).

With this series of RPA derivatives in hand, their efficacy at thermal phosphinidene transfer to 1,3-cyclohexadiene was probed (Scheme 1). All dialkylamide derivatives were found capable of phosphinidene transfer to form 7-phosphanorbornenes RPD (D = C₆H₈ or 1,3-cyclohexadiene), par-



Scheme 1 Thermal phosphinidene transfer from anthracene (“A”) to 1,3-cyclohexadiene (“D”), proposed to proceed through intermediate phosphirane **1** following interception of the free phosphinidene [R₂NP] by the diene.

Table 1 Measurements on RPA thermolysis from heating a 1,3-cyclohexadiene solution to 85 °C, yielding 7-phosphanorbornenes RPD.

RPA	Half-life (h) ^a	RPD Yield ^b
Me ₂ NPA	2.28 ± 0.33	52%
Et ₂ NPA	1.67 ± 0.32	70%
Me ₂ PipPA	0.41 ± 0.13	77%
ⁱ Pr ₂ NPA	0.39 ± 0.06	83%

^a Error listed at the 95% confidence interval

^b Determined by ³¹P NMR spectroscopy by integration against a PPh₃ internal standard

ticularly exciting due to the documented difficulties of metal-assisted aminophosphinidene transfer.²³ Mathey notes that the P–N bond of aminophosphinidene-derived products is a useful tool for further synthetic elaboration, making them desirable derivatives.²³ The relative competency of R₂NPA compounds varied and seemed to correlate positively with steric bulk (see Table 1). The *cis*-2,6-dimethylpiperidide species Me₂PipPA, with a similar steric profile to ⁱPr₂NPA,²⁴ was similarly apt at phosphinidene transfer under the experimental conditions. Contraction to the smaller diethylamide and dimethylamide derivatives led to both retarded RPA fragmentation rate and reduced conversion to RPD. The primary observable side products were tetramers (RP)₄ as detected by ³¹P NMR spectroscopy (SI §S.1.5.3).

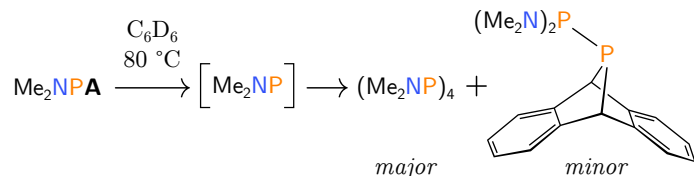
The empirical correlation of ease of phosphinidene transfer with steric properties is likely caused by a series of factors. The larger, electron-rich dialkylamide groups can engage in stronger donation into the P–C σ^* antibonding orbital to facilitate fragmentation. This correlates with stronger π -donation to stabilize the phosphinidene intermediate. Their added steric bulk can also provide kinetic stabilization to the

free phosphinidene, hindering undesired side reactions. Finally, the steric pressure can also increase the entropic push for fragmentation.²⁵

To further probe this hypothesis, we sought to disentangle steric and electronic effects for the amide substituents by analyzing H₂NPA and HMDSP (HMDS = N(SiMe₃)₂)² thermal transfer, the substituents in both cases being less electron releasing than the dialkylamide derivatives but only one being sterically imposing. As it is neither sterically imposing nor strongly electron releasing, parent H₂NPA derivative was anticipated to perform the worst among the two. And in fact, transfer of H₂NP to 1,3-cyclohexadiene was not detected in any appreciable quantity at temperatures up to 105 °C, this system instead forming a white precipitate that was not further characterized. Bulkier HMDSPA was found to successfully form HMDSPD over 14 h at 105 °C in neat 1,3-cyclohexadiene as a mixture with a species we believe to be a phosphirane intermediate **1** (Scheme 1, R = HMDS). Similar phosphirane intermediates have been reported for phosphinophosphinidenes^{13b} and tungsten-bound phosphinidenes.²⁶ The thermal behavior of H₂NPA and HMDSPA reaffirms that sterically bulkier groups improve phosphinidene transfer efficacy when the electronic properties are roughly comparable. Lack of transfer from smaller H₂NPA also serves as circumstantial evidence against bimolecular phosphinidene exchange involving a λ⁵-phosphorane intermediate,²⁷ supporting dissociative production of free aminophosphinidenes from R₂NPA compounds.

Deviation from amide RPA derivatives to substituents less capable of π-donation was found to quell phosphinidene transfer. Heating the chloro, ethoxy, or *tert*-butyl derivatives resulted in no quantifiable transfer to 1,3-cyclohexadiene, though slow anthracene production was observed. Taken together, these data support our conclusion that dialkylamide groups play a major role in successful thermal phosphinidene transfer from RPA species.

Interestingly, though bulkier dialkylamino derivatives exclusively formed *cyclo*-tetraphosphane products²⁸ upon thermalolysis in benzene-*d*₆ in the absence of a trap, Me₂NPA was additionally found to form (Me₂N)₂P-PA as a minor side



Scheme 2 Thermal decomposition of Me₂NPA in the absence of a reaction partner primarily forms (Me₂NP)₄, though other minor byproducts can be observed, including (Me₂N)₂P-PA. This is proposed to proceed through free phosphinidene [Me₂NP].

product (Scheme 2). It was produced in quantities too small for isolation (*ca.* 6%), but its identity could be assigned by NMR spectroscopy (SI §S.1.8). This compound is formally a product of Me₂NP insertion into the P-N bond of another Me₂NPA molecule, a mode of reactivity likely permitted due to the modest size of the methyl substituents. Such a result points towards further phosphinidene reactivity pathways yet to be discovered.²⁹

Molecular Beam Mass Spectrometry. Molecular beam mass spectrometry (MBMS) has been utilized previously by us^{15,19} and others³⁰ to detect reactive small molecules. Such species can be generated using a variety of techniques, our studies taking advantage of the thermal lability of RPA compounds to produce gaseous, reactive small molecules under high vacuum. By entraining these species in an inert buffer gas and avoiding collisions with walls, their transfer from a solid sample to a mass spectrometer can proceed with a diminished propensity for bimolecular or condensation decomposition pathways.

MBMS studies were conducted on each RPA derivative. Monitoring changes to the intensity of the anthracene molecular ion (178 *m/z*) with temperature provided a useful indicator of solid samples of RPA undergoing fragmentation under high vacuum. Upon identification of an appropriate temperature range, inspection of the mass spectra allowed us to search for fragments indicative of concomitant phosphinidene release into the gas phase.

The majority of RPA derivatives were found to liberate significant amounts of anthracene under MBMS conditions starting at *ca.* 120 °C (SI §S.2). The only exceptions were *t*BuPA, which produced limited amounts only upon reaching 160 °C, and H₂NPA, which produced negligible quantities of anthracene up to 200 °C. Unlike the other derivatives, H₂NPA left an orange solid residue within the sample holder following analysis. This residue likely arose from deleterious solid-state chemistry upon heating, possibly through nucleophilic ring-opening polymerization.³¹

Fragments corresponding to the free phosphinidenes were generally observed for the dialkylamide and HMDS derivatives,³² as expected from solution phosphinidene group transfer studies. This is exemplified by the data from MBMS analysis of Me₂NPA (Figure 1). This derivative delivers a clean, gradual release of Me₂NP and anthracene at temperatures up to 157 °C consistent with straightforward fragmentation of the solid precursor. At higher temperatures (160 °C, Figures 1 and S.61), a sharp increase in total ion count was detected reproducibly, and new fragments were observed, including one assigned to the formula (Me₂N)₂P⁺ (119 *m/z*), pointing to intermolecular reactivity, possibly from formation of (Me₂N)₂P-PA or similar compounds *in situ* (*cf.* Scheme 2).

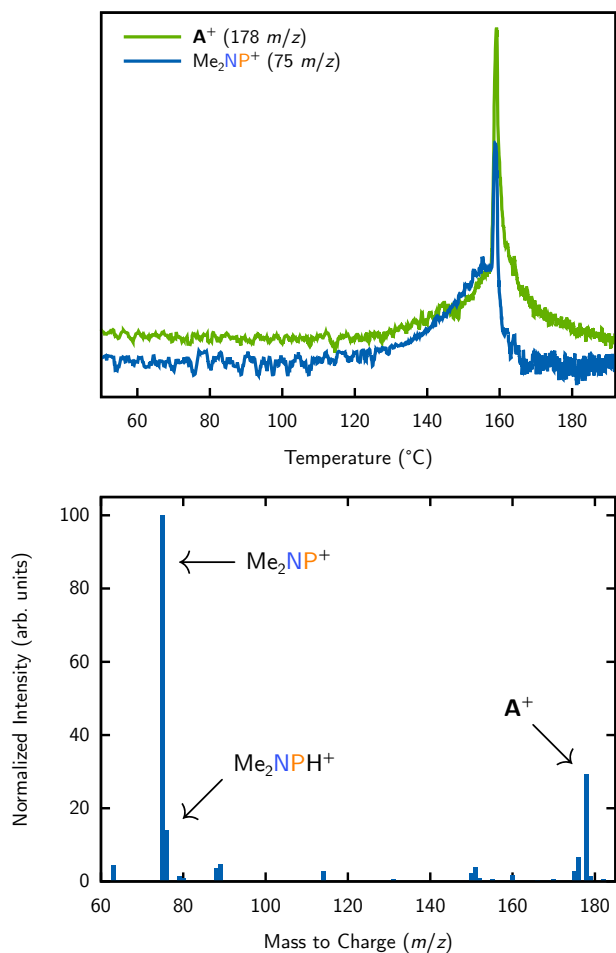


Figure 1 MBMS analysis of Me_2NPA , showing (*top*) the release of anthracene and Me_2NP fragments with temperature, and (*bottom*) the integrated mass fragments over the 132–157 °C range.

Curiously, chlorophosphinidene (ClP^+ 66 m/z) was detected during MBMS analysis of ClPA (SI Figure S.67); this was unexpected as ClP transfer to 1,3-cyclohexadiene was not observed in solution. Unlike most derivatives, the mass spectrum of ClPA also evinced signal for the intact parent molecular ion (ClPA^+ , 244 m/z), suggesting ClP^+ may arise as a fragment of this molecular ion rather than as a consequence of chlorophosphinidene liberation into the gas phase. Indeed, the observation of many species by MBMS analysis of ClPA does not lend itself to detailed interpretation. Similar statements can be made concerning the MBMS analysis of EtOPA , for which the parent molecular ion was also detectable (SI Figure S.66). In all, while gas-phase transport of intact R_2NPA cannot be ruled out, the MBMS data point to thermal fragmentation of the R_2NPA molecular precursors prior to entrainment of neutral R_2NP and **A** into the

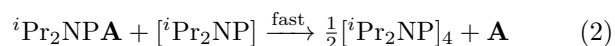
molecular beam with subsequent collisionless transport to the detection chamber.

MBMS conditions for reactive intermediate generation differ greatly from solution thermolysis; as such, these data provide complementary information on the behavior of **RPA** compounds. The proposed clean generation of dimethylaminophosphinidene from Me_2NPA at mild temperatures in particular offers the exciting possibility of direct spectroscopic observation with techniques such as microwave spectroscopy.¹⁵ Such studies are currently underway with the aim to bridge the gap between solution reactivity studies and gas phase spectroscopic and structural characterization.

Eyring Analysis of ${}^i\text{Pr}_2\text{NPA}$ Thermolysis. Though solution **RPA** reactivity appears consistent with generation of a free aminophosphinidene as the key reactive intermediate, alternate mechanistic scenarios certainly can be entertained. It was anticipated that a kinetic analysis would provide further mechanistic insight. Therefore, we investigated the thermal solution kinetic profile of ${}^i\text{Pr}_2\text{NP}$ transfer from anthracene to 1,3-cyclohexadiene, aiming to distinguish between dissociative and associative modes of phosphinidene transfer.³³

Monitoring ${}^i\text{Pr}_2\text{NPA}$ concentration by ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy allowed interrogation of the kinetic profile for this species’s thermal decay under pseudo-unimolecular conditions in neat 1,3-cyclohexadiene (*ca.* 116 equiv). First order decay was seen over the examined temperature range (325–363 K), and an Eyring analysis of the first order rate constants revealed an activation barrier of $\Delta H^\ddagger = 27.3 \pm 1.0$ kcal/mol and $\Delta S^\ddagger = 2.8 \pm 3.0$ cal/mol·K (Figure 2). The first order behavior and the small entropy of activation were indicative of a unimolecular rate determining step, consistent with spontaneous thermal fragmentation of ${}^i\text{Pr}_2\text{NPA}$ into anthracene and unobserved phosphinidene [${}^i\text{Pr}_2\text{NP}$]. To determine the order in the diene reaction partner, the 1,3-cyclohexadiene solvent was gradually diluted with benzene- d_6 (Figure 3). The observed zero order behavior in diene concentration indicates that the diene reaction partner does not participate in the rate-determining step of phosphinidene transfer.

The kinetic behavior of ${}^i\text{Pr}_2\text{NPA}$ thermolysis in the complete absence of 1,3-cyclohexadiene was anomalous. In neat benzene- d_6 at 346 K, the loss of starting material maintained a first order decay profile while the value of k_{obs} roughly doubled from $(19.1 \pm 1.6) \times 10^{-5} \text{ s}^{-1}$ to $(41.1 \pm 2.4) \times 10^{-5} \text{ s}^{-1}$. We propose that in the absence of another trap, thermal decay proceeds as depicted in eqns 1–2.



Assuming rapid reactivity of ${}^i\text{Pr}_2\text{NPA}$ with [${}^i\text{Pr}_2\text{NP}$], application of the steady state approximation to the transient

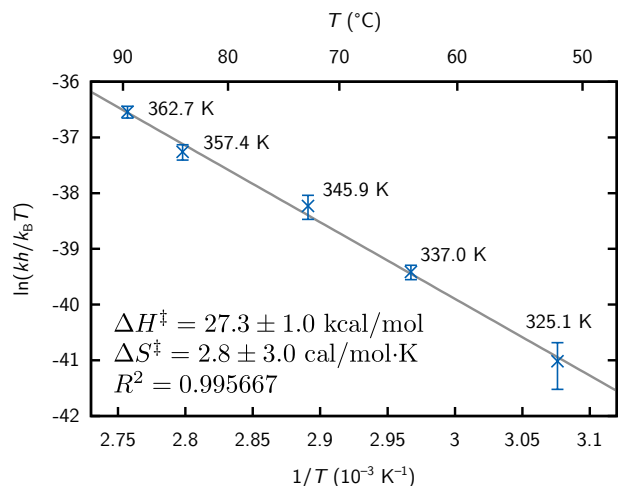


Figure 2 An Eyring plot for thermolysis of $i\text{Pr}_2\text{NPA}$ under pseudo-unimolecular conditions in neat 1,3-cyclohexadiene with error bars shown at the 95% confidence interval using rate constants from monitoring $i\text{Pr}_2\text{NPA}$ decay by ^{31}P NMR spectroscopy.

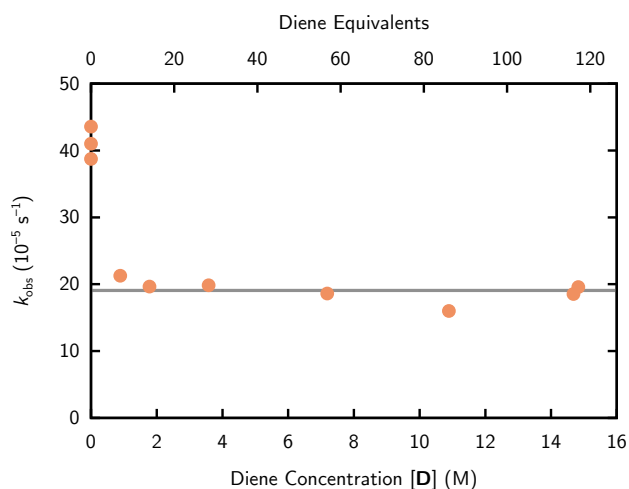


Figure 3 The observed first-order rate constant for $i\text{Pr}_2\text{NPA}$ consumption plotted as a function of 1,3-cyclohexadiene concentration in benzene- d_6 .

phosphinidene successfully predicted a doubling of the rate of consumption of $i\text{Pr}_2\text{NPA}$ compared to that in the presence of a trap, $k_{\text{obs}} \approx 2k_1$.³⁴ Equation 2 is certainly multistep, and the likeliest intermediate in this transformation is bicyclic $(i\text{Pr}_2\text{NP})_2\text{A}$, a species whose identity is consistent with our NMR spectroscopic studies (SI §S.1.9).

Computational Mechanistic Studies. Having in hand information from solution kinetic studies, we next turned to density functional theory (DFT) calculations for further mechanistic insight.³⁵ Following simplification of $i\text{Pr}_2\text{NPA}$

to Me_2NPA , three paths (Figures 4–6) were outlined at the M06-2X³⁶/Def2-TZVP³⁷ level of theory (SI §S.6.1) for formation of the resultant 7-phosphanorbornene species, *anti*- Me_2NPD : a dissociative path *via* the intermediacy of a singlet phosphinidene (Mechanism A), an associative path (Mechanism B), and a dissociative path *via* a triplet phosphinidene (Mechanism C).

Mechanism A, involving generation of a free singlet phosphinidene, was predicted to be the lowest energy pathway for phosphinidene transfer from Me_2NPA to 1,3-cyclohexadiene (Figure 4). Our potential energy surface (PES) scans did not show direct retro-(4+1)-cycloaddition to be operative, as a first-order saddle point for such a transformation could not be located by standard DFT methods (SI §S.6.1.4).³⁸ Instead, phosphinidene release was predicted to be preceded by isomerization, shifting the phosphorus center from bridging the 9,10- to the adjacent 9,9a-positions of the anthracene unit.^{15,39} Retro-(2+1)-fragmentation of the resultant phosphirane intermediate, assisted by rearomatization of anthracene’s central ring, yielded the free singlet phosphinidene, $[\text{Me}_2\text{NP}]$. This fragmentation comprises the rate determining step of formation of *anti*- Me_2NPD via Mechanism A at a cost of $\Delta H^\ddagger = 29.1$ kcal/mol and $\Delta S^\ddagger = -2.2$ cal/mol·K. These values for the activation parameters compare well to those experimentally derived for $i\text{Pr}_2\text{NPA}$.

Singlet $[\text{Me}_2\text{NP}]$ addition to 1,3-cyclohexadiene was found to proceed in a reverse fashion to its release from anthracene: (2+1)-cycloaddition to one C=C bond of 1,3-cyclohexadiene prior to isomerization to yield the ultimate product Me_2NPD . A barrier to the (2+1)-cycloaddition to yield an intermediate phosphirane could not be located by PES scans (SI §S.6.1.6), likely indicative of a nearly barrierless reaction.^{14,40} The proposal of an intermediate phosphirane is in line with our observation by NMR spectroscopy of such a species in the case of HMDSP transfer. Such species also are known for $\text{W}(\text{CO})_5$ -supported phosphinidene addition to 1,3-dienes, where subsequent heating induces isomerization to the 3-phospholene.²⁶ As with concerted Me_2NPA fragmentation, searches using DFT methods for concerted addition of the phosphinidene in a single (4+1)-cycloaddition step to form Me_2NPD did not yield a true transition state (SI §S.6.1.5).³⁸

Barriers to formation of λ^5 -phosphorane intermediates in Mechanism B (Figure 5) were found to be higher than those of Mechanism A. The values of $\Delta\Delta G_{\text{syn}}^\ddagger = 4.0$ kcal/mol and $\Delta\Delta G_{\text{anti}}^\ddagger = 9.9$ kcal/mol reveal that Mechanism A should outcompete Mechanism B. This pathway also demonstrated a clear preference for formation of *syn*- Me_2NPD rather than the observed *anti*- Me_2NPD . Furthermore, the experimentally determined zero order dependence on diene suggests that this associative mechanism can be reasonably excluded.

Dissociative triplet $[\text{Me}_2\text{NP}]$ production (Mechanism C, Figure 6) was also found to proceed along a higher en-

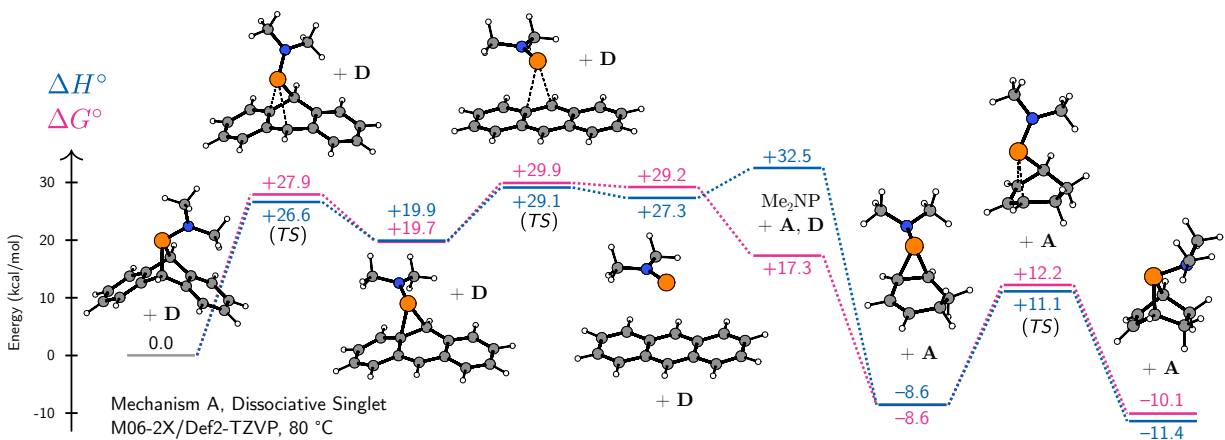


Figure 4 Calculated stationary points and transition states (“TS”) and their relative enthalpies (blue) and free energies (80 °C, red) involved in phosphinidene transfer from Me₂NPA to 1,3-cyclohexadiene through a dissociative singlet mechanism (Mechanism A).

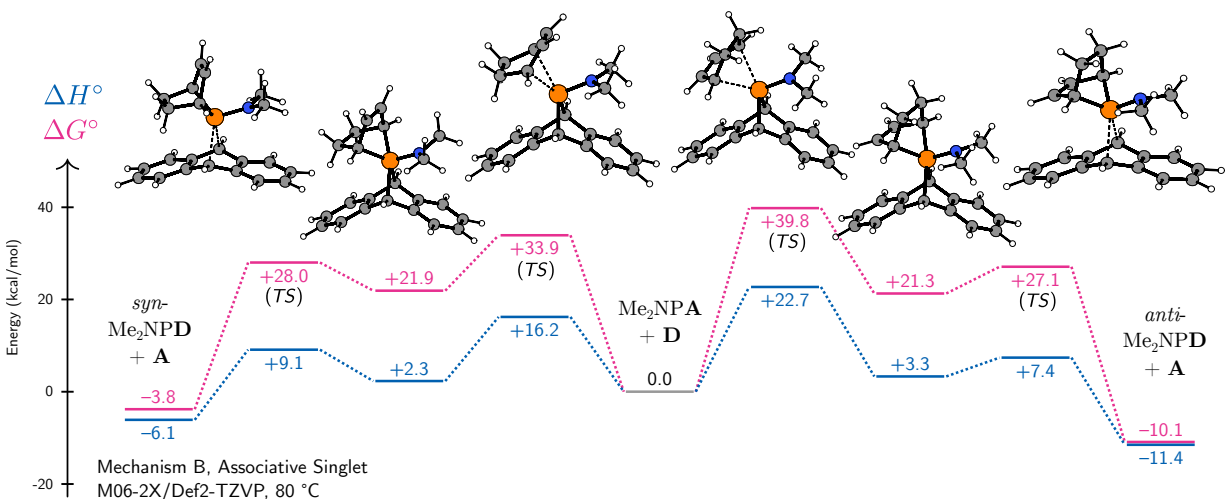


Figure 5 Calculated stationary points and transition states (“TS”) and their relative enthalpies (blue) and free energies (80 °C, red) involved in phosphinidene transfer from Me₂NPA to 1,3-cyclohexadiene through an associative singlet mechanism (Mechanism B).

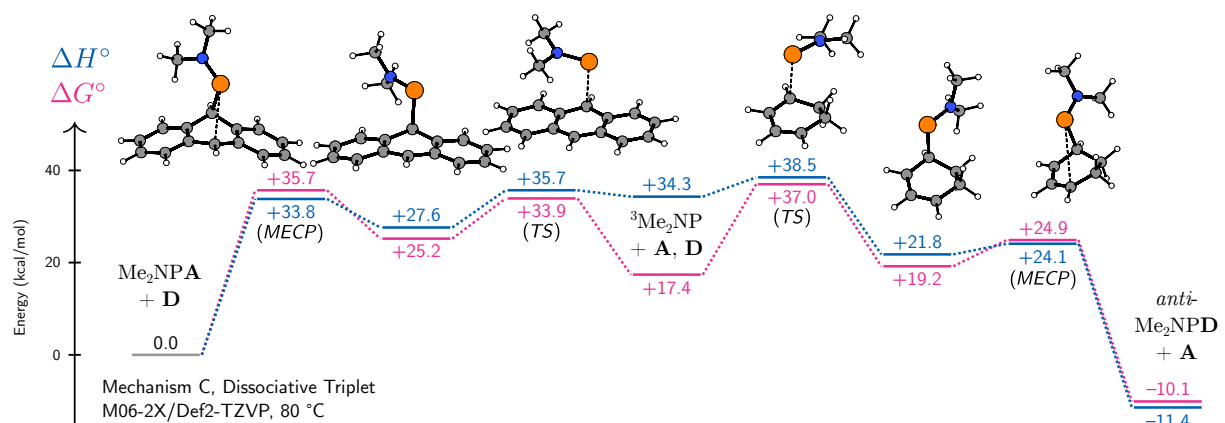


Figure 6 Calculated stationary points, minimum energy crossing points (“MECP”), and transition states (“TS”) and their relative enthalpies (blue) and free energies (80 °C, red) involved in phosphinidene transfer from Me₂NPA to 1,3-cyclohexadiene through a dissociative triplet mechanism (Mechanism C).

ergy pathway than Mechanism A. With a rate limiting step of $\Delta G^\ddagger = 37.0$ kcal/mol and two instances of intersystem crossing, this pathway was deemed an unlikely mechanism for phosphinidene transfer from anthracene to 1,3-cyclohexadiene. The relatively large barrier for $^3[\text{Me}_2\text{NP}]$ addition to 1,3-cyclohexadiene ($\Delta G^\ddagger = 19.6$ kcal/mol) is also notable, contrasting with the nearly barrierless singlet analog. Concerted release of $^3[\text{Me}_2\text{NP}]$ through a retro-(4+1)-cycloaddition pathway was deemed unlikely, as the triplet PES was uniformly higher than the singlet PES (SI §S.6.1.4). It is also implausible that such a triplet mechanism would yield the observed *syn/anti* stereospecificity. A singlet biradicaloid intermediate can also be excluded due to the high-energy nature of open-shell singlet $[\text{Me}_2\text{NP}]$ (*vide infra*).

Phosphinidene Bonding Analysis. It was unsurprising that dialkylamide substituents proved paramount to successful phosphinidene transfer, as amino- and phosphinophosphinidenes have been computationally predicted to be among the most stable.¹⁸ As such, the bonding of dialkylaminophosphinidene $[\text{Me}_2\text{NP}]$ deserves further comment.

Amide π -donation to the phosphorus center was found to dramatically influence the ground spin state. Though many phosphinidenes are predicted to have a triplet ground state, substituents capable of strong π -donation break the degeneracy of the two p orbitals on phosphorus, altering the singlet-triplet energy gap.¹⁸ State-averaged CASSCF(6,4)-NEVPT2⁴¹ calculations⁴² predicted a closed-shell singlet ground state with a triplet and open-shell singlet lying 3.9 and 20.8 kcal/mol uphill, respectively. Such a small singlet-triplet gap (ΔE_{ST}) likely gives rise to the singlet reactivity, as singlet reactions should outcompete intersystem crossing to a triplet state, paralleling the chemistry of carbenes with small singlet-triplet gaps.⁴³

This strong π -donation lends itself well to analysis by natural bond orbital (NBO) methods. Similar to N -heterocyclic carbenes (NHCs) and phosphinophosphinidenes,⁴ π -donation from the adjacent nitrogen center into the nominally subvalent element center's empty p orbital results in a full octet of electrons. One would expect that for any one-coordinate phosphorus center to be stable, it should achieve an octet through multiple bonding to its substituent. This is demonstrated well using a natural resonance theory (NRT) analysis,⁴⁴ revealing a N=P natural bond order of 1.98 with the lone dominant (91.53% weight) Lewis structure involving a N=P double bond (Figure 7). This bond is strongly polarized towards the nitrogen center, and in combination with a π_{NP}^* antibonding orbital polarized towards the phosphorus, results in reactivity expected of an electrophilic subvalent phosphorus center. The electrophilicity of the phosphinidene is reflected in the Laplacian of its electron density ($\nabla^2\rho$) by Quantum Theory of Atoms in Molecules (QTAIM) analysis⁴⁵

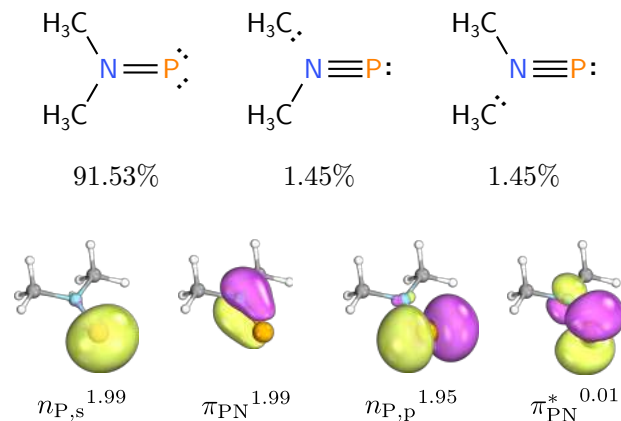


Figure 7 (*top*) Dominant Lewis structures for singlet phosphinidene $[\text{Me}_2\text{NP}]$ by NBO NRT analysis. (*bottom*) Relevant natural bond orbitals shown with orbital occupancies.

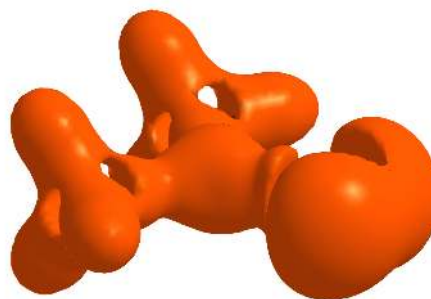


Figure 8 The zero surface of the Laplacian of the electron density ($\nabla^2\rho = 0$) for singlet phosphinidene $[\text{Me}_2\text{NP}]$ by QTAIM analysis.

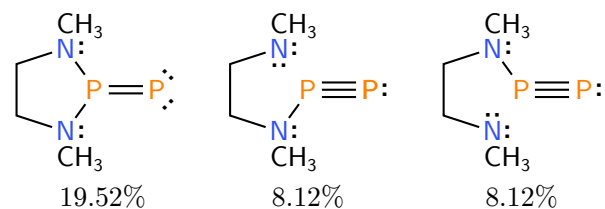


Figure 9 Dominant Lewis structures of a model of Bertrand's phosphinophosphinidene.

(Figure 8), where regions both of rapid density accumulation and depletion can be seen about the phosphorus center.

It is interesting to compare the $\text{N}\cdots\text{P}$ bond order of Me_2NP with the $\text{P}\cdots\text{P}$ bond order of the recently reported isolable phosphinophosphinidene of Bertrand.⁴ An NRT analysis on a model compound (Figure 9) reveals a 2.40 natural bond order⁴⁶ between the phosphorus centers, increased from that of Me_2NP likely as a consequence of decreased polarization

across the P=P bond. Additionally, the high electronegativity of nitrogen leads to in-plane phosphorus lone pair donation into N-P σ^* orbitals and consequently an increased importance of “no-bond” resonance contributors such as the ones that provide 8.12% in Figure 9. Reflections of these differing bonding patterns are certain to be uncovered in the reactivities of amino- and phosphinophosphinidenes, and are already manifest in their cycloaddition reactivity with 1,3-cyclohexadiene.¹³

Cycloaddition with Olefins and Alkynes. To pursue unsaturated reaction partners beyond 1,3-dienes, we undertook the study of R₂NP transfer to electron-rich olefin acceptors, known to react productively with ^tBu₂PP.¹³ Heating a solution of Me₂PipPA in neat cyclohexene to 75 °C for 4 h led to detection of a single new major species by ³¹P{¹H} NMR spectroscopy in 64% yield with a diagnostic chemical shift⁴⁷ of δ -117 ppm. Further NMR spectroscopic experiments confirmed the identity of this new product to be *anti,cis*-Me₂PipPC₆H₁₀ (Scheme 3), obtained as a single isomer concomitantly with anthracene production.

Crystallization provided pure Me₂PipPC₆H₁₀ as a colorless solid in 44% isolated yield. Analysis by X-ray crystallography further corroborated that the piperidine and cyclohexane rings are positioned on opposite faces of the phosphirane ring (Figure 10). The phosphirane features an acute CPC angle of 47.21(7)° and P-C bonds of 1.877 Å (avg), a value typical for a single phosphorus-carbon bond. This can be compared with 7-phosphanorbornadienes, which have a significantly wider CPC angle (*ca.* 79°) but two slightly elongated P-C bonds (*ca.* 1.91 Å).² The present synthesis of *anti,cis*-phosphirane Me₂PipPC₆H₁₀ through Me₂PipP interception by cyclohexene is also reminiscent of the proposed mechanism of R₂NP addition to 1,3-cyclohexadiene *via* an intermediate phosphirane.

The stereoselectivity of this cycloaddition was unexpected, as phosphinidene cycloaddition to olefins has been predicted to be barrierless⁴⁰ or nearly so.¹⁴ Additionally, though not explicitly discussed in the original reports, phosphinophosphinidene cycloaddition to olefins seems to share this stereoselectivity.^{4,13} We sought to investigate computationally whether this phenomenon is kinetically or thermodynamically controlled; however, DFT PES scans have not uncovered transition states for *syn* or *anti* (2+1)-cycloaddition between Me₂NP and cyclohexene at the M06-2X/Def2-TZVP level of theory (SI §S.6.3). This difficulty may reflect particularly low barriers and shallow energy wells for the encounter complexes, or it could be a consequence of the barriers being largely entropic in nature.⁴⁸ Further studies pursuing variational transition state searches⁴⁹ are planned to clarify the existence and nature of these barriers.

If nonzero, any such barriers to (2+1)-cycloaddition

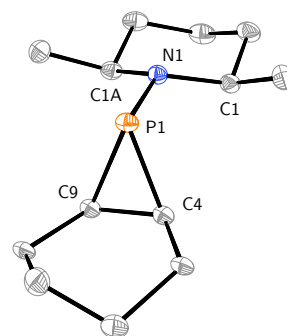
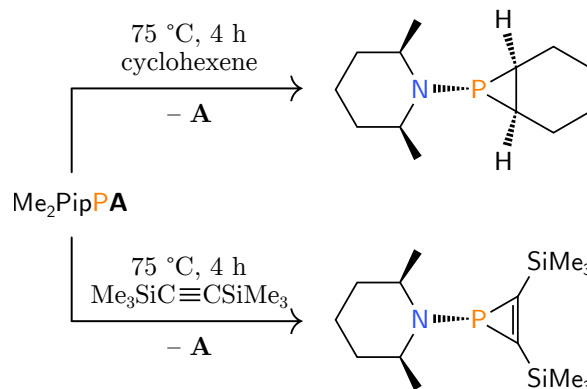


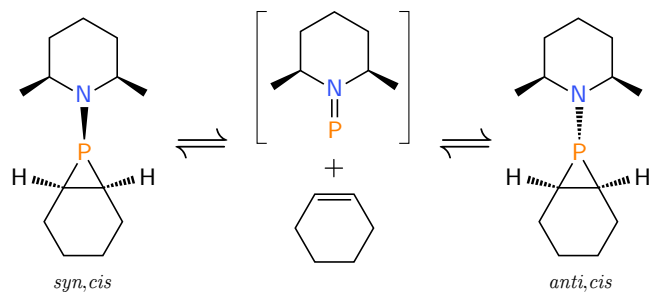
Figure 10 Solid-state molecular structure of *anti,cis*-Me₂PipPC₆H₁₀ with ellipsoids at the 50% probability level. Hydrogen atoms and second domain of the disordered cyclohexane ring are omitted for clarity. Selected interatomic distances (Å) and angles (°): P1-C 1.877 (avg), P1-N1 1.7364(8), C1-N1 1.4794(7); N1-P1-C4 108.5(3), N1-P1-C9 105.0(2), C4-P1-C9 47.21(7), C1-N1-C1A 115.29(7), C1-N1-P1 116.50(4).

between dialkylaminophosphinidenes and cyclohexene are bound to be small. Thus, the stereoselectivity is likely under thermodynamic rather than kinetic control, as the *syn*-isomer is predicted to be uphill by *ca.* 2 kcal/mol (SI §S.6.3). Such a suggestion would require an equilibrium between the isomers, possibly through the free phosphinidene (Scheme 4). A similar equilibration may also control formation of *anti/syn*-7-phosphanorbornenes RPD (SI §S.6.4). Both the cyclohexene and 1,3-cyclohexadiene products are unlikely to equilibrate through direct phosphine inversion, as the barriers are predicted to be prohibitively endergonic (SI §S.6.4.1).⁵⁰

Earlier claims of thermal aminophosphinidene generation from *P*-aminophosphiranes and related three-membered rings can be found in the literature.^{3,51} Accordingly, we de-

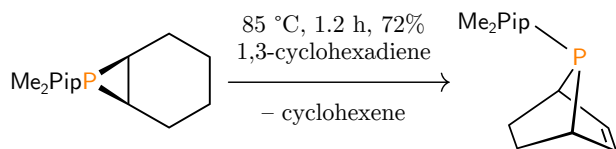


Scheme 3 Phosphinidene transfer from Me₂PipPA to cyclohexene to form phosphirane *anti,cis*-Me₂PipPC₆H₁₀ or to bis(trimethylsilyl)acetylene to form phosphirene Me₂PipPC₂(SiMe₃)₂.



Scheme 4 Proposed stereochemical equilibration between the *syn,cis* and *anti,cis* stereoisomers of $\text{Me}_2\text{PipPC}_6\text{H}_{10}$.

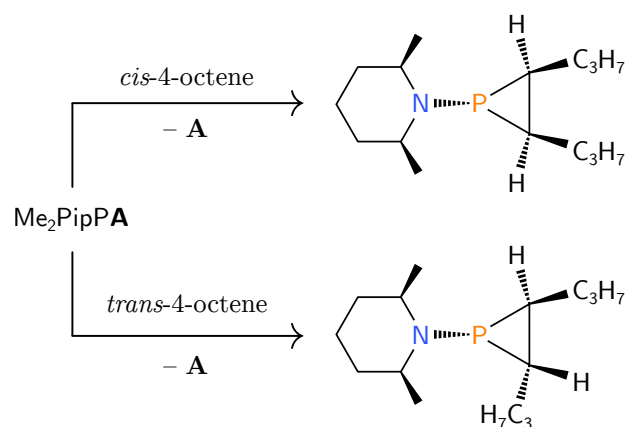
cided to investigate the possibility of thermal aminophosphinidene transfer from $\text{Me}_2\text{PipPC}_6\text{H}_{10}$ to 1,3-cyclohexadiene (Scheme 5). Monitoring a solution of *anti,cis*- $\text{Me}_2\text{PipPC}_6\text{H}_{10}$ in neat 1,3-cyclohexadiene at 85 °C for 1.2 h by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy gave an affirmative result: 65% formation of *anti*- Me_2PipPD . Phosphinidene transfer from *anti,cis*- $\text{Me}_2\text{PipPC}_6\text{H}_{10}$ to 1,3-cyclohexadiene supports the hypothesis of phosphinidene exchange as a means of stereochemical equilibration to the thermodynamic product. Further studies are necessary to establish the scope and mechanism of phosphinidene transfer from phosphiranes.



Scheme 5 Phosphinidene transfer from cyclohexene to 1,3-cyclohexadiene as quantified by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Similar to cyclohexene cycloaddition, thermolysis of a saturated solution of Me_2PipPA in neat bis(trimethylsilyl)acetylene at 75 °C for 4 h gave phosphirene formation in 72% yield as quantified by ^{31}P NMR spectroscopy (Scheme 3 and SI §S.1.7). This was somewhat surprising due to the documented thermal instability of phosphirenes.⁵² The success of this phosphinidene transfer may lie in the particular choice of alkyne, as its trimethylsilyl groups should have a stabilizing effect in the face of molecular strain. Lacking silyl groups, 2-hexyne and tolane were not found to be competent phosphinidene acceptors under these conditions.

Skell Hypothesis. The success of phosphinidene transfer to cyclohexene also permitted performance of a convenient experiment to test for the spin state of a putative intermediate phosphinidene. The Skell Hypothesis,⁵³ initially applied to carbenes, asserts that a mechanism involving a free singlet carbene as the key reactive intermediate should proceed through a concerted cheletropic step and retain stereochemistry of the olefin; whereas, a mechanism involving a triplet



Scheme 6 Stereospecific cycloaddition supporting singlet phosphinidene transfer by the Skell hypothesis.

carbene intermediate should proceed by stepwise addition to the olefin and result in stereochemical scrambling. As such, the stereospecificity of cycloaddition is a useful probe for the spin state of the presumed reactive intermediate. *Cis*- and *trans*-4-octene were selected as substrates for this test.

Heating a saturated solution of Me_2PipPA in neat *cis*-4-octene to 75 °C for 3 h resulted in 64% conversion to a single phosphirane by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy with a chemical shift of -116 ppm. The ^1H NMR spectrum of this product showed clear C_s symmetry, consistent with stereospecific cycloaddition. Further 2D and multinuclear NMR experiments supported formation of the *anti,cis*-isomer, signifying retention of olefin stereochemistry.

Similarly, heating a saturated solution of Me_2PipPA in neat *trans*-4-octene to 75 °C for 3 h gave 51% conversion to a single phosphirane distinct from the last ($^{31}\text{P}\{^1\text{H}\}$ δ -97 ppm). Extensive 2D and heteronuclear NMR spectroscopic experiments allowed assignment of this C_1 -symmetric phosphirane as the *anti,trans*-product of stereospecific cycloaddition to *trans*-4-octene. Successful stereochemical phosphinidene transfer to both isomers of 4-octene without any trace of scrambling is consistent with the intermediacy of a singlet phosphinidene.

The lack of stereochemical scrambling highlights the synthetic utility of singlet phosphinidenes over their triplet counterparts. Most commonly, photolysis of traditional phosphinidene precursors has given transfer to alkynes, alkenes, or 1,3-dienes with little specificity and stereochemical control over the identity of the products. For example, irradiation of the phosphirane MesPC_2H_4 in the presence of 1,3-cyclohexadiene was reported to yield both the *syn*- and *anti*-isomers of the resulting MesPC_6H_8 phosphirane, among other products.⁵⁴ This is likely due to the biradical nature of the extruded phosphinidene intermediate and the lack of equilibration to the thermodynamic product. Thus, singlet phos-

phosphinidene generation from R₂NPA compounds is a useful method for the formation of phosphiranes with enhanced control over product stereochemistry.⁵⁵

Conclusions

Dibenzo-7-phosphanorbornadiene compounds have been demonstrated to be competent, thermally activated transfer reagents for aminophosphinidenes. Although the substituent scope for successful RPA fragmentation to generate free phosphinidenes is limited to amides, dialkylamide derivatives in particular have proven to be exceedingly versatile. Our results point to singlet [R₂NP] transfer through a dissociative mechanism, further substantiated by DFT calculations. Broadening the range of unsaturated reaction partners beyond 1,3-cyclohexadiene helps to solidify phosphinidenes' newfound position in the synthetic chemist's toolbox. The P–N bond in the resultant products also provides a convenient handle for further functionalization²³ to access additional phosphines. Work in our group is ongoing to capitalize upon phosphinidene transfer from RPA thermolysis to expedite synthesis of value-added phosphorus compounds, including chiral phosphines and transition metal phosphinidene complexes.

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Supplemental Information

Experimental details, characterization data, X-ray crystallographic information, computational details, and tables of Cartesian coordinates are provided in the Supporting Information document.

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