P,N Ligands

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Facile Synthesis of Phosphaamidines and Phosphaamidinates using Nitrilium Ions as an Imine Synthon**

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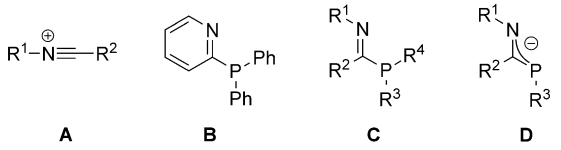
In memory of Fritz Bickelhaupt

Abstract: *Readily accessible nitrilium triflates are convenient imine building blocks for the expedient synthesis of a novel class of 1,3-P,N ligands as demonstrated for the reaction with primary phosphanes. This procedure allows variation of all substituents. X-ray crystal structures are reported for nitrilium ions, phosphaamidines, and three phosphaamidinate complexes. The lithium phosphaamidinate is N coordinated and its reaction with [AuCl(tht)] (tht = tetrahydrothiophene) gives a unique P-bridged gold trimer, while a P,N-bidentate complex results from [{RhCl(cod)}$_2$]. The nitrilium ion methodology allows extension of the 1,3-P,N motive to bis(imino)phosphanes, which are the neutral phosphorus analogues of the valuable β-diketiminate ligand.*

The nitrilium ions **A**[1] are reactive intermediates in a number of classic organic reactions, such as the Beckmann rearrangement,[2] the Ritter,[3] and the Ugi reaction.[4] The isolation of the first stable nitrilium salts was reported by both Klages and Grill[5] and Meerwein et al.[6] in 1955, but the development and application of these imine synthons has remained rather limited, likely for practical reasons. For example, the commonly used Lewis acid $SbCl_5$ for conversion of imidoyl chlorides into nitrilium salts is toxic,[5,7] and the alternative approach to alkylate nitriles suffers from the limited availability of trialkyloxonium salts (i.e., Meerwein's reagent $R_3O^+BF_4^-$, R = Me, Et).[1,6,8,9]



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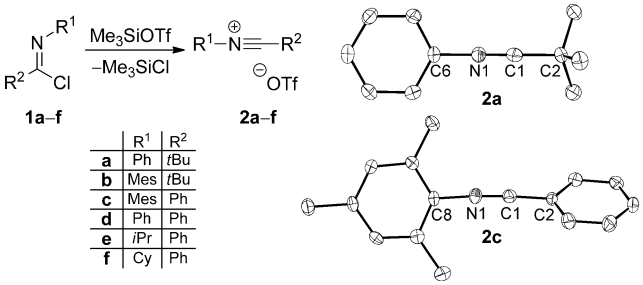
We were keen on developing a scalable and efficient synthesis of a range of nitrilium ions and exploring their use in the preparation of 1,3-P,N ligands.[10] The archetypical P,N ligand 2-pyridyldiphenylphosphane (**B**) has found widespread application in coordination chemistry and catalysis[10c,11] in spite of its structurally limited N-donor site.[12] Iminophosphanes (i.e., phosphaamidines **C**), in contrast, offer an easily tunable imine fragment which allows facile steering of the steric and electronic properties of the ligand, but they are difficult to access. So far, only four examples were prepared by reacting an imidoyl chloride[13,14] with alkali-metal phosphides[15] or silylphosphanes.[16,17] Two additional reports mention the synthesis of bis(imino)phosphanes, but without conclusive analytical data.[15b,18] Moreover, convenient synthetic access to the phosphorus analogues of the highly versatile and much used amidinate ligands,[19] that is, the anionic phosphaamidinates **D**,[15c,16,20] is not available other than by using silylphosphanides and nitriles.[20d,21] Herein we report the synthesis of nitrilium triflates and their reactivity toward primary phosphanes,[22] which allows the facile synthesis of **C**, **D**, and bis(imino)phosphanes.

The reaction of the imidoyl chlorides **1a–f** with trimethylsilyl triflate (TMSOTf) in CH_2Cl_2 afforded the nitrilium triflates **2a–f** as sole products after removal of all volatiles (Scheme 1).[23] The N-aryl-substituted nitrilium triflates **2a–d** were readily purified by crystallization on a multigram scale (78–99%) and proved to be stable at room temperature under

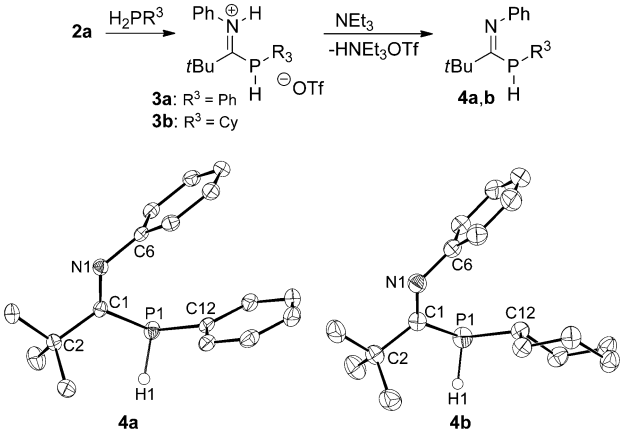


	R^1	R^2
a	Ph	*t*Bu
b	Mes	*t*Bu
c	Mes	Ph
d	Ph	Ph
e	*i*Pr	Ph
f	Cy	Ph

Scheme 1. Synthesis of the nitrilium triflates **2a–f** and molecular structures of **2a** and **2c** (hydrogen atoms and the noncoordinating OTf anion are omitted for clarity, and displacement parameters are drawn at 50% probability level. For **2c** one of the two crystallographic independent cations is shown). Selected bond lengths [Å] and angles [°] for **2a**: N1–C1 1.125(3), N1–C6 1.402(2), C1–C2 1.461(3); C1-N1-C6 179.3(2), N1-C1-C2 177.7(2). **2c** (values for the second cation in square brackets): N1–C1 1.140(4) [1.142(4)], N1–C8 1.412(4) [1.405(4)], C1–C2 1.423(4) [1.431(4)]; C1-N1-C8 176.1(3) [176.0(3)], N1-C1-C2 177.6(4) [174.8(3)].

an inert atmosphere. In contrast, the N-alkyl-substituted salts **2e**,**f** are thermally labile, albeit storable for months at −80 °C. The molecular structures of **2a** and **2c** were established unequivocally by X-ray crystal structure determinations (Scheme 1).[24] They showed a linear conformation of the nitrilium ion with a typical N≡C bond [**2a**: 1.125(3), **2c**: 1.140(4) Å] which compares well with the only other structurally characterized N-aryl-substituted nitrilium salt, that is, $[2,6\text{-}Me_2C_6H_4\text{-}N{\equiv}C\text{-}Me][BF_4]$.[25,26]

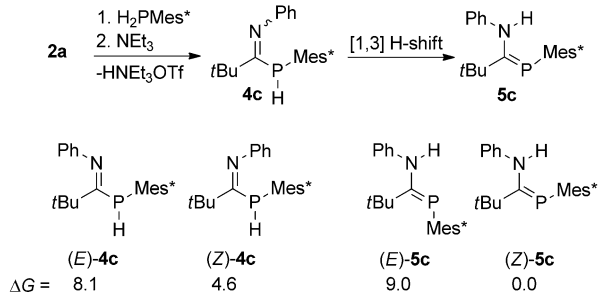
To explore the reactivity of the nitrilium triflates, we examined the reaction of **2a** with primary phosphanes both experimentally and computationally. Treatment of **2a** with phenyl- and cyclohexylphosphane for 10 minutes at −78 °C afforded, quantitatively, the respective iminium triflates **3a** and **3b** [**3a**: $\delta^{31}P = -50.5$ ppm, $^1J(P,H) = 255.6$ Hz; **3b**: $\delta^{31}P = -29.0$ ppm, $^1J(P,H) = 243.2$ Hz] by P-nucleophilic attack on the nitrilium ion followed by a [1,3] H-shift from phosphorus to the more basic nitrogen site (Scheme 2). Subsequent



Scheme 2. Synthesis of the phosphaamidines **4a**,**b** and molecular structures of **4a**,**b** (hydrogen atoms are omitted for clarity, except for H1, one crystallographic independent molecule of **4b** is shown, and displacement parameters are drawn at 50% probability level). **4b** crystallizes with two crystallographic independent molecules in the asymmetric unit of which the values of the second are within square brackets. Selected bond lengths [Å] and torsion angles [°] for **4a**: P1–C1 1.8748(13), P1–H1 1.325(15), N1–C1 1.2720(16), N1–C6 1.4159(16); P1-C1-N1-C6 −1.21(17). **4b**: P1–C1 1.8631 (13) [1.8648 (15)], P1–H1 1.330(14) [1.324(14)], N1–C1 1.2760(16) [1.2736(18)], N1–C6 1.4166(17) [1.4115(18)]; P1-C1-N1-C6 −0.72(18) [-0.39(19)].

addition of triethylamine at −78 °C afforded, after work-up, in good yield the secondary iminophosphanes **4a** [85%; $\delta^{31}P = -64.7$ ppm, $^1J(P,H) = 231.9$ Hz] and **4b** [79%; $\delta^{31}P = -42.7$ ppm, $^1J(P,H) = 220.8$ Hz] as colorless solids. Single-crystal X-ray diffraction analysis revealed unequivocally a *Z*-configurated imine (Scheme 2) with C=N bond character [**4a**: 1.2720(16), **4b**: 1.2736(18) Å] and a typical P–C bond [**4a**: 1.8748(13), **4b**: 1.8648(15) Å].[24] The *E* conformers of **4a**,**b** were not detected by ^{31}P NMR spectroscopy, and concurs with the DFT calculations at the ωB97X-D/6-31 + G(d,p)[27] level of theory, and indicates these *E* isomers to be the least stable ones [$\Delta G_{E\text{-}Z} = 5.4$ (**4a**), 2.2 (**4b**) kcal mol^{-1}].

Treatment of the nitrilium triflate **2a** with 2,4,6-tri-*tert*-butylphenylphosphane (Mes^*PH_2) and subsequently with



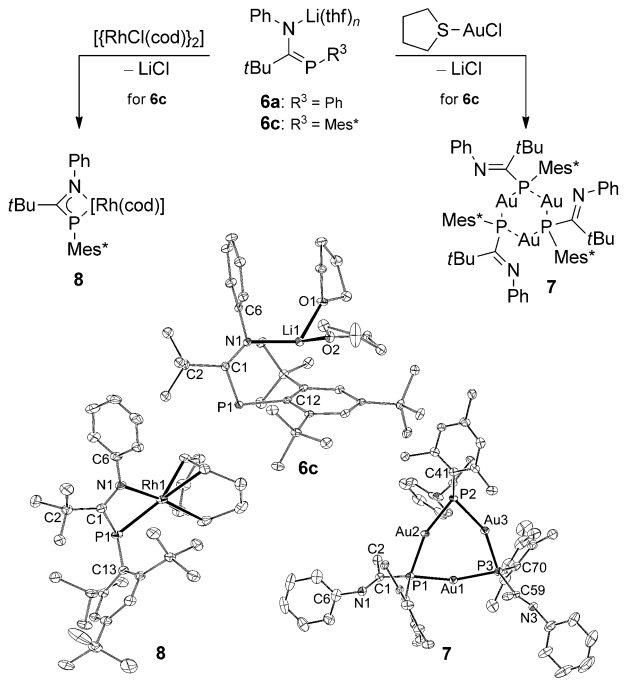
Scheme 3. Formation of **4c** and **5c** (top) and the computed isomers of *E*/*Z*-**4c** and *E*/*Z*-**5c** at ωB97X-D/6-31 + G(d,p) level of theory (bottom).

NEt_3 afforded two isomers of the iminophosphane **4c** in a 3:2 ratio [$\delta^{31}P$: −55.3 ppm, $^1J(P,H) = 243.2$ Hz and −56.7 ppm, $^1J(P,H) = 252.9$ Hz; Scheme 3]. Both isomers tautomerized under the reaction conditions to the aminophosphaalkene **5c**, which was isolated as a yellow oil in 88% yield [$\delta^{31}P = 102.0$, $\delta^{1}H = 5.26$ (N*H*) ppm].[28,29] Calculations at the ωB97X-D/6-31 + G(d,p)[27] level of theory showed (*Z*)-**5c** to be the thermodynamic product of this reaction [$\Delta G =$ 8.1 ((*E*)-**4c**), 4.6 ((*Z*)-**4c**), 9.0 ((*E*)-**5c**), and 0.0 ((*Z*)-**5c**) kcal mol^{-1}; Scheme 3, bottom],[30] and compares well with the reported (*Z*)-DippP=C(*p*-$CH_3C_6H_4$)N(H)Dipp (Dipp = 2,6-*i*$Pr_2C_6H_3$) by Boeré and co-workers.[20b] These findings illustrate that a diverse set of P,N ligands is accessible by simply changing the substituents.

Having the phosphaamidines **4a**,**b** and **5c** in hand, we explored the synthesis and coordination chemistry of the corresponding phosphaamidinates. Treatment of either **4a** or **5c** with *n*-butyl lithium at −78 °C in THF provided the orange-colored **6** in good yield upon isolation (**6a**: 86%, $\delta^{31}P = 10.9$ ppm; **6c**: 66%, $\delta^{31}P = 38.6$ ppm; Scheme 4). The molecular structure of the Mes*-derivative **6c** (Scheme 4), obtained by a single-crystal X-ray structure determination,[24] shows an N-coordinated lithium ion [Li1-N1 2.013(4) Å] bearing two molecules of thf and an interaction with the Mes* ring [i.e., Li1-C12 2.599(4) Å]. The elongated *Z*-configured P=C bond [P1-C1 1.750(2) Å] and shortened N–C bonds [N1-C1 1.327(3) Å] are indicative of a delocalized 1-aza-3-phosphaallyl system as was highlighted by Niecke et al.[20a]

Our next step was to establish the coordination modes for the phosphaamidinate ligand with transition metals, since no such complexes have been reported in the literature.[31] A soft metal should favor P coordination, which is indeed the case, but with an unexpected result. Reaction of **6c** with [AuCl(tht)] at room temperature afforded **7** as yellow crystals (66%, $\delta^{31}P = -7.8$ ppm; Scheme 4). Its molecular structure displays a unique gold(I) phosphanyl trimer with a six-membered $\{P_3Au_3\}$ core [e.g., Au1-P1 2.354(2) Å] and three noncoordinating *E* imine substituents [e.g., N1-C1 1.269(9); Scheme 4].[24] The P-Au-P angles are distorted from linearity [e.g., P1-Au1-P3 155.35(7)°] and the $\{Au_3\}$ triangle features Au···Au distances of 3.0168(6), 3.0945(6), and 3.1030(6) Å,[32] which are similar to the ones found for $[\{Au(PIs_2)\}_3]$ (Is = 2,4,6-*i*$Pr_3C_6H_2$) as reported by Glueck et al.[33]

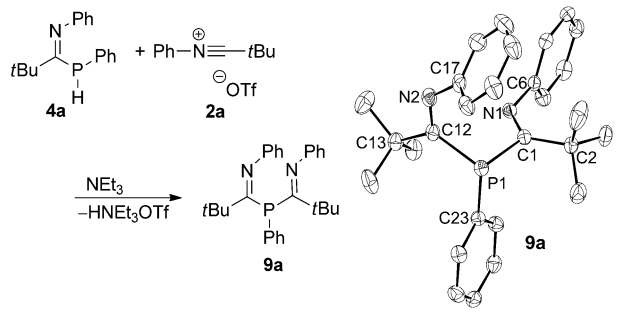
Next, we targeted the P,N-chelating motif for transition metals,[34] as this is the predominant bonding mode in the



Scheme 4. Preparation of the phosphaamidinates **6a**,**c**, gold complex **7**, and rhodium complex **8** (top), and the molecular structures of **6c**, **7**, and **8** [bottom; disordered atoms, hydrogen atoms, and solvent molecules (and the methyl groups of the *tert*-butyl groups for **7**) are omitted for clarity, and displacement parameters are drawn at 50% probability level. For **7** only one of the two crystallographic independent molecules is shown]. Selected bond lengths [Å] and angles [°] for **6c**: P1–C1 1.750(2), P1–C12 1.871(2), N1–C1 1.327(3), N1–Li1 2.013(4), Li1–C6 2.723(4), Li1–C12 2.599(4). **7**: Au1–P1 2.354(2), Au1–P3 2.339(2), Au1–Au2 3.0168(6), Au1–Au3 3.1030(6), Au2–Au3 3.0945(6), P1–C1 1.848(8), N1–C1 1.269(9); P1-Au1-P3 155.35(7). **8**: Rh1-P1 2.3513(6), Rh1-N1 2.085(2), P1-C1 1.820(2), N1-C1 1.309(3); P1-C1-N1 103.15(15), P1-Rh1-N1 67.41(5).

widely applied, analogous *N*,*N*′-amidinates.[19] To this end, we treated **6c** with the rhodium complex [{RhCl(cod)}$_2$] to obtain the anticipated **8** as an orange solid [82%, δ^{31}P = −45.3 ppm, ^1J(P,Rh) = 64.4 Hz; Scheme 4]. The molecular structure of **8** shows a κ^2-phosphaamidinate complex [Rh1-P1 2.3513(6), Rh1-N1 2.085(2) Å] bearing a η^4-coordinated cod fragment and features a shortened P−C bond [P1-C1 1.820(2) Å], an elongated N=C bond [N1-C1 1.309(3) Å], and a P1-Rh1-N1 angle of 67.41(5)° (Scheme 4). This bite angle is larger than that for the corresponding amidinate ligands (63°)[35] because of the larger size of the P atom, which will have an effect on its reactivity,[36] and is currently under investigation.

Finally, we explored whether the nitrilium ion methodology would allow extending the 1,3-P,N ligand with a second imine unit to potentially give 1,3,5-N,P,N ligands. Treatment of **4a** with **2a** and NEt$_3$ afforded the bis(imino)phosphane **9a** as a yellow solid in 92% yield (δ^{31}P = 17.0 ppm; Scheme 5, left).[23] A single-crystal X-ray analysis confirmed the unique structure of **9a** (Scheme 5),[24] which contains an intact (*Z*)-**4a** moiety [N2−C12 1.262(3) Å] with an additional *E* imine (N1−C1 1.270(3) Å). The structure represents the first fully characterized neutral, phosphorus analogue of the valuable β-diketiminate ligand family.[37]



Scheme 5. Synthesis of the bis(imino)phosphane **9a** and its molecular structure (only one of the two crystallographic independent molecules is shown, hydrogen atoms are omitted for clarity, and displacement parameters are drawn at 50% probability level). Selected bond lengths [Å] (values for the second cation in square brackets): P1–C1 1.858(2) [1.880(2)], P1–C12 1.890(2) [1.882(2)], N1–C1 1.270(3) [1.268(3)], N2–C12 1.262(3) [1.274(3)].

In conclusion, we have shown that readily accessible nitrilium triflates are very convenient building blocks for the synthesis of novel classes of phosphaamidines, phosphaamidinates, and bis(imino)phosphanes, thus allowing variation of all substituents. The full potential of these readily available P,N ligands in coordination chemistry and catalysis is currently being explored in our laboratories.

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[1] a) S. Kanemasa, *Sci. Synth.* **2004**, *19*, 53 – 66; b) A. Hegarty, *Acc. Chem. Res.* **1980**, *13*, 448 – 454.
[2] a) E. Beckmann, *Ber. Dtsch. Chem. Ges.* **1886**, *19*, 988 – 993; b) S. Yamabe, N. Tsuchida, S. Yamazaki, *J. Org. Chem.* **2005**, *70*, 10638 – 10644.
[3] a) J. J. Ritter, P. P. Minieri, *J. Am. Chem. Soc.* **1948**, *70*, 4045 – 4048; b) R. W. Darbeau, R. S. Pease, E. V. Perez, R. E. Gibble, F. A. Ayo, A. W. Sweeney, *J. Chem. Soc. Perkin Trans. 2* **2002**, 2146 – 2153.
[4] a) I. Ugi, *Angew. Chem.* **1962**, *74*, 9 – 22; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 8 – 21; b) N. Chéron, R. Ramozzi, L. El Kaïm, L. Grimaud, P. Fleurat-Lessard, *J. Org. Chem.* **2012**, *77*, 1361 – 1366.
[5] F. Klages, W. Grill, *Justus Liebigs Ann. Chem.* **1955**, *594*, 21 – 32.
[6] a) H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert, K. W. Müller, H. J. Sasse, H. Schrodt, J. Spille, *Angew. Chem.* **1955**, *67*, 374 – 380; b) H. Meerwein, P. Laasch, R. Mersch, J. Spille, *Chem. Ber.* **1956**, *89*, 209 – 224.
[7] $AlCl_3$ can also be used as Cl-abstracting agent to generate nitrilium salts, see: a) D. Hall, P. K. Ummat, K. Wade, *J. Chem. Soc. A* **1967**, 1612 – 1615, but their cation reactivity in organic synthesis is typically hampered by the reactivity of the $AlCl_4$ anion. For the use of the toxic $SnCl_4$, see: b) R. Madroñero, S. Vega, *Synthesis* **1987**, 628 – 630.
[8] "Triethyloxonium Tetrafluoroborate" H. Perst, D. G. Seapy in *Encyclopedia of Reagents for Organic Synthesis*, Wiley, New York, **2008**, pp. 1 – 9.
[9] Alternative alkylating agents are: a) MeOTf, see: B. L. Booth, K. O. Jibodu, M. F. Proença, *J. Chem. Soc. Chem. Commun.* **1980**, 1151 – 1153; b) Me_3SiCH_2OTf, see: K. Matsuo, Y. Matsuo,

A. Iwashita, E. Nakamura, *Org. Lett.* **2009**, *11*, 4192 – 4194; c) a combination of $SbCl_5$ and alkyl halides, see: ref. [6b] and J. Gordon, G. Turrell, *J. Org. Chem.* **1959**, *24*, 269 – 271; d) $FeCl_3$ and alkyl halides, see: R. Fuks, D. Baudoux, C. Piccinni-Leopardi, J.-P. Declercq, M. Van Meerssche, *J. Org. Chem.* **1988**, *53*, 18 – 22.

[10] a) A. Pfaltz, W. J. Drury III, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5723 – 5726; b) P. J. Guiry, C. P. Saunders, *Adv. Synth. Catal.* **2004**, *346*, 497 – 537; c) S. Maggini, *Coord. Chem. Rev.* **2009**, *253*, 1793 – 1832.

[11] a) G. R. Newkome, *Chem. Rev.* **1993**, *93*, 2067 – 2089; b) Z.-Z. Zhang, H. Cheng, *Coord. Chem. Rev.* **1996**, *147*, 1 – 39; c) P. Espinet, K. Soulantica, *Coord. Chem. Rev.* **1999**, *193 – 195*, 499 – 556.

[12] a) E. Drent, P. Arnoldy, P. H. M. Budzelaar, *J. Organomet. Chem.* **1993**, *455*, 247 – 253; b) A. Brück, K. Ruhland, *Organometallics* **2009**, *28*, 6383 – 6401; c) L. Hintermann, T. T. Dang, A. Labonne, T. Kribber, L. Xiao, P. Naumov, *Chem. Eur. J.* **2009**, *15*, 7167 – 7179.

[13] Ethyl *N*-arylformimidates can also be used. See: M. Song, B. Donnadieu, M. Soleilhavoup, G. Bertrand, *Chem. Asian J.* **2007**, *2*, 904 – 908.

[14] Imidoyl chlorides only react directly with non-activated phosphanes under very harsh reaction conditions (e.g. 150 °C for 4 days). See Ref. [20b].

[15] a) K. Issleib, O. Löw, *Z. Anorg. Allg. Chem.* **1966**, *346*, 241 – 254; b) J. Heinicke, A. Tzschach, *Z. Chem.* **1978**, *18*, 452 – 453; c) X. Li, H. Song, C. Cui, *Dalton Trans.* **2009**, 9728 – 9730; for 2,3-bis-phosphino-1,4-diazadienes, see: d) D. Walther, S. Liesicke, L. Böttcher, R. Fischer, H. Görls, G. Vaughan, *Inorg. Chem.* **2003**, *42*, 625 – 632; e) D. Walther, S. Liesicke, R. Fischer, H. Görls, J. Weston, A. Batista, *Eur. J. Inorg. Chem.* **2003**, 4321 – 4331; for a related synthesis toward 2,4-diazaphospholides, see: D. Stein, T. Ott, H. Grützmacher, *Z. Anorg. Allg. Chem.* **2009**, *635*, 682 – 686.

[16] K. Issleib, H. Schmidt, H. Meyer, *J. Organomet. Chem.* **1978**, *160*, 47 – 57. For the use of α-chloroiminium chlorides, see: A. Schmidpeter, A. Willhalm, *Angew. Chem.* **1984**, *96*, 901 – 902; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 903 – 904.

[17] For miscellaneous routes to phosphaamidines, see: a) N. Merceron, K. Miqueu, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **2002**, *124*, 6806 – 6809; b) T. Saegusa, Y. Ito, N. Yasuda, T. Hotaka, *J. Org. Chem.* **1970**, *35*, 4238 – 4340; c) A. Haas, K. Peterman, *J. Fluorine Chem.* **1986**, *30*, 439 – 453.

[18] G. V. Romanov, T. Y. Ryzhikova, A. N. Pudovik, *Zh. Obshch. Khim.* **1990**, *60*, 1718 – 1722.

[19] a) F. T. Edelmann, *Adv. Organomet. Chem.* **2008**, *57*, 183 – 352; b) F. T. Edelmann, *Adv. Organomet. Chem.* **2013**, *61*, 55 – 374.

[20] a) K. Paasch, M. Nieger, E. Niecke, *Angew. Chem.* **1995**, *107*, 2600 – 2602; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2369 – 2371; b) R. T. Boeré, M. L. Cole, P. C. Junk, J. D. Masuda, G. Wolmershäuser, *Chem. Commun.* **2004**, 2564 – 2565; c) G. Becker, J. R. Heck, U. Hübler, W. Schwarz, E.-U. Würthwein, *Z. Anorg. Allg. Chem.* **1999**, *625*, 2008 – 2024; d) Z.-X. Wang, D.-Q. Wang, J.-M. Dou, *J. Organomet. Chem.* **2003**, *665*, 205 – 213, and references therein; e) G. Becker, G. Ditten, K. Hübler, U. Hübler. K. Merz, M. Niemeyer, N. Seidler, M. Westerhausen, Z. Zheng in *Organosilicon Chemistry II: From Molecules to Materials* (Eds.: N. Auner, J. Weis), Verlag Chemie, Weinheim, **1996**, p. 161.

[21] a) M. Westerhausen, M. H. Digeser, W. Schwarz, *Inorg. Chem.* **1997**, *36*, 521 – 527; b) M. Westerhausen, M. H. Digeser, W. Schwarz, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1237 – 1242.

[22] For the reactivity of N nucleophiles toward nitrilium salts, see, for example, Ref. [9a].

[23] See the Supporting Information for details.

[24] CCDC 983061 (**2a**), 983062 (**2c**), 983063 (**4a**), 999177 (**4b**), 983064 (**6c**), 983065 (**7**), 983066 (**8**), and 983067 (**9a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[25] A. K. Gjøystdal, C. Rømming, *Acta Chem. Scand. Ser. B* **1977**, *31*, 56 – 62.

[26] For an N-alkyl-substituted nitrilium salt, see: a) O. V. Bykhovskaya, I. M. Aladzheva, P. V. Petrovskii, M. Y. Antipin, Y. T. Struchkov, T. A. Mastryukova, M. I. Kabachnik, *Mendeleev Commun.* **1993**, *3*, 200 – 202; for structurally characterized metal-based nitrilium ions, see: b) C. P. Casey, M. Crocker, G. P. Niccolai, P. J. Fagan, M. S. Konings, *J. Am. Chem. Soc.* **1988**, *110*, 6070 – 6076; c) S. A. MacLaughlin, J. P. Johnson, N. J. Taylor, A. J. Carty, E. Sappa, *Organometallics* **1983**, *2*, 352 – 355; d) S. Doherty, G. Hogarth, M. Waugh, T. H. Scanlan, W. Clegg, M. R. J. Elsegood, *Organometallics* **1999**, *18*, 3178 – 3186.

[27] a) J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615 – 6620; b) J.-D. Chai, M. Head-Gordon, *J. Chem. Phys.* **2008**, *128*, 084106. DFT calculations were carried out with Gaussian 09 (Revision A.02); see the Supporting Information.

[28] For other reports on amino-phosphaalkenes, see: a) Ref. [20a,b]; b) L. Boubekeur, L. Ricard, P. Le Floch, N. Mézailles, *Organometallics* **2005**, *24*, 3856 – 3863, and references therein; c) R. Appel, F. Knoll, I. Ruppert, *Angew. Chem.* **1981**, *93*, 771 – 784; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 731 – 744.

[29] Note that one of first thermally stable phosphaalkenes was reported by F. Bickelhaupt and co-workers. See: T. C. Klebach, R. Lourens, F. Bickelhaupt, *J. Am. Chem. Soc.* **1978**, *100*, 4886 – 4888.

[30] ωB97X-D/6-31 + G(d,p) calculations for the P-phenyl-substituted **4a** and **5a** confirmed that (*Z*)-**4a** is the most stable structure [$\Delta G = 0.0$ ((*Z*)-**4a**), 5.4 ((*E*)-**4a**), 5.7 ((*Z*)-**5a**), and 11.8 ((*E*)-**5a**) kcal mol^{-1}].

[31] Only a κ^2-phosphaamidinate platinum(II) complex has been postulated by Issleib et al. See Ref. [16].

[32] H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2012**, *41*, 370 – 412.

[33] a) D. M. Stefanescu, H. F. Yuen, D. S. Glueck, J. A. Golen, A. L. Rheingold, *Angew. Chem.* **2003**, *115*, 1076 – 1078; *Angew. Chem. Int. Ed.* **2003**, *42*, 1046 – 1048; b) D. M. Stefanescu, H. F. Yuen, D. S. Glueck, J. A. Golen, L. N. Zakharov, C. D. Incarvito, A. L. Rheingold, *Inorg. Chem.* **2003**, *42*, 8891 – 8901.

[34] So far, only κ^2-*P,N*-phosphaamidinate complexes are structurally characterized for Li, K, and Sn. See: Ref. [20d], as well Ref. [21] for Mg, Ca, Sr, and Ba.

[35] For related rhodium(I) amidinate complexes, see: a) F. J. Lahoz, A. Tiripicchio, M. T. Camellini, L. A. Oro, M. T. Pinillos, *J. Chem. Soc. Dalton Trans.* **1985**, 1487 – 1493; b) J. R. Hagadorn, J. Arnold, *J. Organomet. Chem.* **2001**, *637 – 639*, 521 – 530; c) C. Jones, D. P. Mills, A. Stasch, *Dalton Trans.* **2008**, 4799 – 4804.

[36] Z. Freixa, P. W. N. M. van Leeuwen, *Dalton Trans.* **2003**, 1890 – 1901.

[37] a) L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031 – 3065; b) Y.-C. Tsai, *Coord. Chem. Rev.* **2012**, *256*, 722 – 758.

