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Bis(imino)phosphanes: Synthesis and Coordination Chemistry

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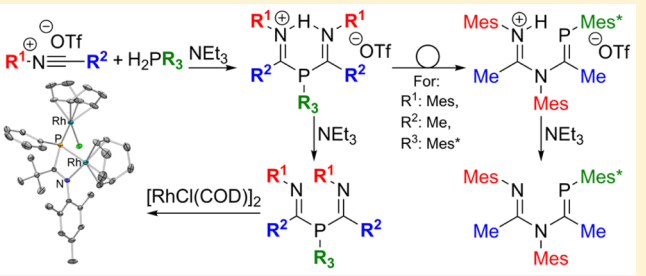
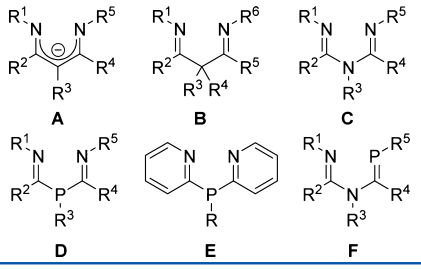
Supporting Information

ABSTRACT: Bis(imino)phosphanes can be synthesized efficiently from iminophosphanes and nitrilium triflates, allowing for nonsymmetric substitution at the imine groups. Symmetrically substituted derivatives can even be obtained in a one-pot procedure from primary phosphanes. These potential N,N-bidentate ligands are sensitive toward Cu(II), Zn(II), and rhodium(I) sources, resulting in loss of an imine group. For $[RhCl(COD)]_2$ this led to an N,P- and P-chelating bimetallic complex. Bis(imino)phosphanes with C-Me substituents rearrange *in situ* to unique 1,3,5-phosphadiazapentadienes for which a P-coordinated gold(I) complex is reported. The bis(imino)phosphanes are readily oxidized to stable bis(imino)-phosphane oxides with aqueous H_2O_2.

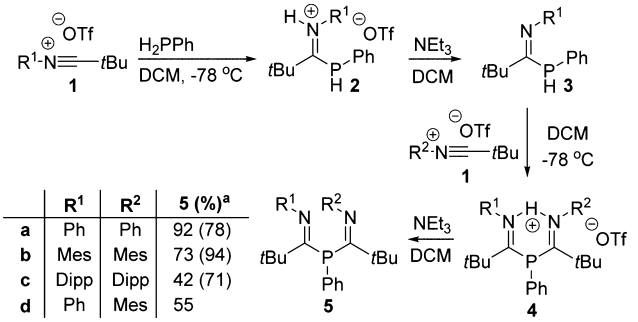


INTRODUCTION

Anionic β-diketiminates (**A**) are established N,N-bidentate ligands for homogeneous catalysis,[1] but the neutral β-diimines (**B**)[2] are not despite their potential in nickel- and palladium-catalyzed polymerizations of ethylene[3] and in the Heck, Suzuki, and Hiyama coupling reactions.[4] In contrast, the neutral triazapentadienes (**C**)[5] in which a nitrogen atom instead of a carbon atom separates the imine groups show ample N,N-dichelating ability,[6] besides that of the amine group.[7] Rare though are the related bis(imino)phosphanes (**D**),[8] in which the imine groups are separated by a phosphorus atom, albeit that dipyridylphosphanes (**E**), having pyridine instead of imine groups, are known N,N-[9] and N,P-bidentate[10] and P-monodentate ligands.[9a,10f,k,11] Because of the limited access to bis(imino)phosphanes **D**, which may carry different substituents at the P, N, and C sites, we thought it relevant to explore their scope and limitations. In this study, we extend our recent work on 1,3-P,N-ligands[12] and elaborate on the synthesis of N,P,N-ligands including an efficient one-pot procedure, explore their coordination chemistry, report on their rearrangement to an unprecedented 1,3,5-phosphadiazapentadiene (**F**), and also address their oxidizability.



Scheme 1. Synthesis of Bis(imino)phosphanes[a]



	R¹	R²	5 (%)[a]
a	Ph	Ph	92 (78)
b	Mes	Mes	73 (94)
c	Dipp	Dipp	42 (71)
d	Ph	Mes	55

[a]Yields from **3** and from H_2PPh in parentheses.

RESULTS AND DISCUSSION

Synthesis. Bis(imino)phosphanes can be synthesized from nitrilium triflates and iminophosphanes, which in turn are readily obtained from a nitrilium ion and a phosphane (Scheme 1). Recently, we reported on this methodology for the synthesis of 1,3-N,P-ligands and their anions, using a range of phosphane and nitrilium ion substituents, and showed their suitability for transition metal complexation.[12] In addition, we provided a

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single example of a 1,3,5-N,P,N-ligand (**5a**; R^1, R^2 = Ph), generated from the 1,3-N,P-precursor **3a**,[12a] on which we expand here. For example, reaction of the yellow solid **3b** (R^1 = Mes; δ ^{31}P −59.7 (d, ^1J(P,H) = 235.3 Hz)), obtained from phenylphosphane and *N*-mesityl,*tert*-butyl nitrilium triflate **1b** after deprotonation of their adduct **2b** (δ ^{31}P −46.5 (d, ^1J(P,H) = 263.6 Hz)), with another equivalent of **1b** in DCM at −78 °C resulted in the formation of **4b** (δ ^{31}P −36.1 (s)), which upon deprotonation with triethylamine, filtration over alumina, and crystallization from pentane at −20 °C afforded a single isomer of **5b** (δ ^{31}P 11.8 (s)) in 73% yield. The same product could even be obtained in 94% yield by means of a simple *one-pot procedure* using H_2PPh and 2.5 equiv of the nitrilium salt **1b**; in comparison, executing the same one-pot procedure using nitrilium salt **1a** gave 78% of the reported *E,Z*-**5a**. The observed single singlet in the ^{31}P NMR spectrum of **5b** supports the formation of only its *E,Z*-isomer. Calculations at ωB97X-D/6-31+G(d,p) revealed a ΔG preference of 0.8 kcal·mol^{-1} for this isomer over the *E,E*-isomer, which is in harmony with the formation of *E,Z*-**5a**, as was established by an X-ray structure.[13] Intriguingly though, the protonated precursor **4b** favors a conformation with a nonsymmetrically N-*H*-N-bridged proton that connects the two *E*-imine groups (calc d_{NH} 1.074, 1.574 Å). This *E,E*-conformer is energetically favored over the two nonbridged N-protonated isomers of *E,Z*-**4b** by ΔG 5.5 (*Z*-NH) and 7.1 (*E*-NH) kcal·mol^{-1} as well as over the P-protonated *E,E*-isomer (12.9 kcal·mol^{-1}). It then appears that there is a conformational change on deprotonating **4b** to **5b**.

Using the same procedure, freshly synthesized iminophosphane **3c** (R^1 = Dipp, δ ^{31}P −60.0 (d, ^1J(P,H) = 237.8 Hz), 88%) reacted with nitrilium triflate **1c** (R^2 = Dipp) to give instead mainly the P-protonated intermediate (δ ^{31}P −43.5 ppm (d, ^1J(P,H) = 269.5 Hz)) and only a trace of its N-protonated isomer **4c** (δ ^{31}P −8.3 ppm (s)). Subsequent *in situ* deprotonation resulted exclusively in bis(imino)phosphane *E,Z*-**5c** (R^1, R^2 = Dipp; δ ^{31}P 10.8 (s)) in 42% yield after crystallization from pentane at −20 °C. The one-pot procedure using H_2PPh and 2.5 equiv of **1c** resulted in an increased yield of 71% for *E,Z*-**5c**; its calculated ΔG preference over the *E,E*-isomer amounts to 1.5 kcal·mol^{-1}. Interestingly, asymmetrically N-*H*-N-bridged intermediate **4c** (calc d_{NH} 1.069, 1.578 Å) is favored over its P-protonated *E,Z*-isomer by a significant 10.5 kcal·mol^{-1}, which seemingly contrasts the observations and therefore suggests slow tautomerization between the isomeric intermediates.

The stepwise nitrilium ion methodology allows for the synthesis of nonsymmetrically substituted bis(imino)-phosphanes. For example, reacting imino(phosphane) **3a** (R^1 = Ph) with nitrilium salt **1b** (R^2 = Mes) gave bridged N,N-protonated iminium adduct **4d** (δ ^{31}P 40.2 (s); calc d_{NH} 1.094, 1.508 Å), which fully converted upon deprotonation to a single isomer of the nonsymmetrically substituted bis(imino)-phosphane **5d** (R^1 = Ph, R^2 = Mes; δ ^{31}P 17.9 (s)) in an isolated yield of 55%. The molecular structure of **5d** (Figure 1), established by a single-crystal X-ray structure determination,[13] shows unequivocally an *E*(Ph),*Z*(Mes)-conformation for the two imine groups with C6−N1−C1−P1 and C17−N2−C12−P1 dihedral angles of 176.27(10)° and −4.6(2)°, respectively; (Ph) and (Mes) refer to the imine groups carrying the indicated substituents. DFT calculations confirm the *E*(Ph),*Z*(Mes)-isomer to be the most stable one, with ΔG differences of 3.8 and 2.2 kcal·mol^{-1} with the *E*(Mes),*Z*(Ph)- and *E*(Mes),*E*(Ph)-isomers, respectively. The lengths of the

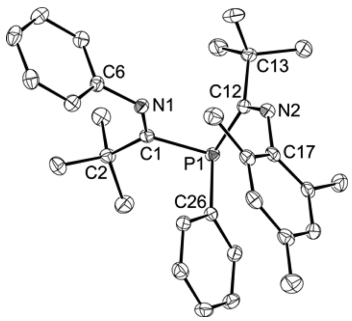
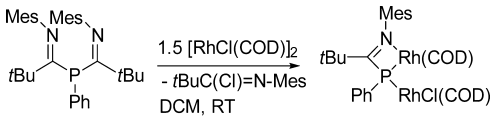


Figure 1. Displacement ellipsoid plot of bis(imino)phosphane **5d** at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), angles (deg), and torsion angles (deg): C1−N1 1.2767(16), C1−P1 1.8770(13), C12−N2 1.2697(17), C12−P1 1.8749(13), C26−P1 1.8374(13), N1−C1−P1 114.54(9), N2−C12−P1 130.30(10), C6−N1−C1−P1 176.27(10), C17−N2−C12−P1−4.6(2).

imine bonds of **5d** (C1−N1 = 1.2767(16), C12−N2 = 1.2697(17) Å) are very similar to those of both **5a** (d_{av} 1.269 Å) and **3a** (1.2720(16) Å).[12a]

Coordination Chemistry. Comparison of the transition metal chelation of bis(imino)-phosphane **5b** with that of triazapentadienes and dipyridylphosphanes shows significant differences. Exemplary is the Mo complexation using $MoI_2(CO)_3(MeCN)_2$, which gives an N,N′-complex with Py_2PhP (**E**),[9c] but its mixing with **5b** in $CDCl_3$ resulted in an unstable product (≤15%; δ ^{31}P 50.1) that could not be isolated; heating to 65 °C to increase the conversion led only to decomposition. Likewise, ^{31}P NMR monitoring of the interaction of **5b** with Cu(II) and Zn(II) salts,[14] used for N,N′-coordination of triazapentadienes,[6a] showed only decomposition with formation of imino-phosphane **3b**. These experiments suggest a sensitivity of the 1,3,5-N,P,N-ligand toward transition metal induced dissociation, which was further substantiated on Rh complexation. Monitoring the reaction of **5b** with $[RhCl(COD)]_2$ in $CDCl_3$ by ^{31}P NMR spectroscopy showed full conversion to a single product with a triplet at δ −13.7 ppm (J(P,Rh) = 104.0 Hz) on using 1.5 equiv of the Rh complex. Isolation, crystallization by slow diffusion of Et_2O into a DCM solution, and ^{1}H, ^{13}C, and ^{31}P NMR analysis suggested that bimetallic complex **6** had formed (97% yield) with loss of an imine group from **5b**, which concurs with the determined mass of m/z 768.1478 (M + H) (Scheme 2).

Scheme 2. Synthesis of Dirhodium Complex 6



5b **6**

The molecular structure of **6** (Figure 2), obtained by a single-crystal X-ray structure determination,[13] shows a unique bimetallic complex of which the phosphaamidine N,P-coordinates to a Rh(COD) moiety (N1−Rh2 = 2.0959(16) Å, P1−Rh2 = 2.3299(6) Å) with additional coordination of the phosphorus center to Rh(COD)Cl (P1−Rh1 = 2.2972(6) Å). Both P−Rh bonds are shorter than in the bridging phosphide rhodium complex $[\{Rh(COD)\}_2(\mu\text{-Cl})(\mu\text{-}t\text{Bu}_2\text{P})]$ (2.364(3), 2.368(3) Å).[15] The C1−P1 bond length of 1.880(2) Å falls

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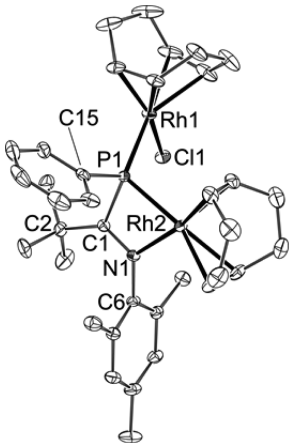
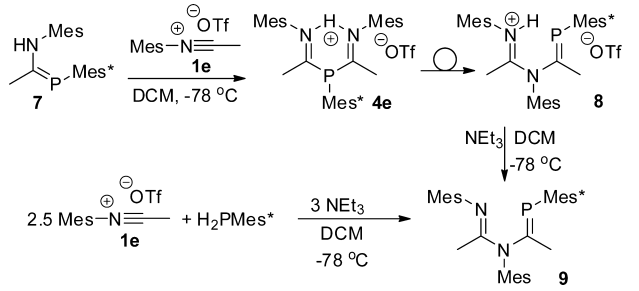


Figure 2. Displacement ellipsoid plot of dirhodium complex **6** at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å), angles (deg), and torsion angles (deg): C1−N1 = 1.292(3), C1−P1 = 1.880(2), C1−C2 = 1.535(3), N1−C6 = 1.445(2), N1−Rh2 = 2.0959(16), P1−C15 = 1.845(2), P1−Rh1 = 2.2972(6), P1−Rh2 = 2.3299(6), Rh1−Cl1 = 2.3975(6), C1−N1−Rh2 = 106.77(12), C1−P1−Rh2 = 81.22(6), N1−C1−P1 = 103.12(13), P1−C1−N1−Rh2 = −0.42(14).

within the expected range for a single bond and is similar to those of iminophosphane **4a** (1.8748(13) Å)[12a] and bis(imino)phosphanes **5a** (d_{av} 1.878 Å)[12a] and **5d** (d_{av} 1.876 Å). The length of the C1−N1 imine bond of 1.292(3) Å falls within the range expected for a N=C double bond but is slightly longer than those of **4a** (1.2720(16) Å),[12a] **5a** (d_{av} 1.269 Å),[12a] and **7** (d_{av} 1.273 Å). The structure of **6** confirms that Mes−N=C(Cl)−*t*Bu and 0.5 equiv of $[RhCl(COD)]_2$ are lost on reacting the Rh complex with **5b**; the ^{1}H NMR spectrum of the two components resembles the observed signals in the spectrum of the crude reaction mixture of **6**.

Rearrangement. We wondered whether the intermediate ion **4** plays a role in the dissociation of **5** to its precursor **3**. In exploring this aspect, we found the ion to be susceptible to rearrangement. This was established for the reaction of 1,3-aminophosphaalkene **7** (instead of iminophosphane **3** (see Scheme 1)) with *C*-methyl,*N*-mesityl nitrilium triflate **1e** (Scheme 3). Whereas the expected *E,E*-**4e** ion was instantly

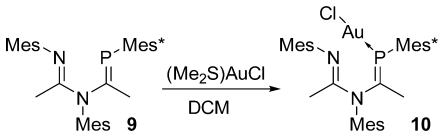
Scheme 3. Synthesis of Phosphadiazapentadiene 9



identified by its ^{31}P NMR resonance at δ 11.3 ppm (the *E,Z*-isomer is 20.4 kcal·mol^{-1} less stable), it rearranged over time with full conversion in 120 h to give a singlet at δ 174.6 ppm. This resonance is indicative of a phosphaalkene and suggests the formation of P,N,N-intermediate *E,E*-**8**. The DFT calculations support this course of events. Not only do they show a ΔG preference for the *E,E*-ion over its *E(P),Z(N)*- and *E(N),Z(P)*-isomers of 9.0 and 11.4 kcal·mol^{-1}, respectively, they also reveal it to be favored by a significant 7.8 kcal·mol^{-1} over its N,P,N-isomeric precursor *E,E*-**4e**. Subsequent treatment of the solution with NEt_3 to deprotonate the ion furnished the unique 1,3,5-phosphadiazapentadiene *E,E*-**9**[16] (δ ^{31}P 188.9; the *E,E*-isomer is favored over the *E(P),Z(N)* and *(E(N),Z(P)* by 2.1 and 2.4 kcal·mol^{-1}, respectively). The DFT calculations show that *E,E*-**9** is thermodynamically favored over the N,P,N-isomeric bis(imino)phosphane (**5e**) by a substantial ΔG of 10.1 kcal·mol^{-1}. Because of its strong thermodynamic preference *E,E*-**9** is conveniently, cleanly, and quantitatively obtained in a one-pot procedure from H_2PMes* and an excess of nitrilium triflate **1e** in DCM at −78 °C without showing a trace of **5e**.

Reaction of *E,E*-**9** with (Me_2S)AuCl in DCM gave full conversion to the P-coordinated AuCl complex **10** (Scheme 4).

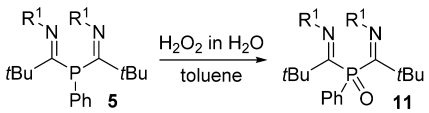
Scheme 4. Gold(I) Coordination to Phosphaalkene 9



The complexation causes a 59.5 ppm shielding to give a ^{31}P NMR chemical shift at δ 129.4 ppm, which is characteristic for phosphaalkene coordination to AuCl.[17] Unfortunately, due to its thermal instability, we were unable to obtain crystals suitable for an X-ray crystal structure analysis.

Oxidizability. In spite of their intriguing chemistry, bis(imino)-phosphanes appear sensitive to dissociation and rearrangement. Modifying the phosphorus center to a phosphane oxide is an obvious step to enhance their stability. To our surprise, this could be accomplished under harsh oxidative Brønsted acidic conditions. For example, stable phosphane oxides were simply obtained by vigorously mixing a toluene solution of **5** with a 11.5 M aqueous solution of H_2O_2 (Scheme 5). Isolation and crystallization from diethyl ether at

Scheme 5. Oxidation of Bis(imino)phosphanes



	R^1	%
11b	Mes	78
11c	Dipp	95

−20 °C afforded **11b** (δ ^{31}P 22.8 (s)) and **11c** (δ ^{31}P 22.8 (s)) in yields of 78% and 95%, respectively. Although it is beyond the scope of the present study, these new readily accessible bis(imino)phosphane oxides, allowing diverse substitution patterns, are likely valid new N,N-bidentate ligands and potentially alternatives to bis(acyl)phosphane oxides for use as photoinitiators in radical polymerizations.[18]

CONCLUSION

In summary, nonsymmetrically substituted bis(imino)-phosphanes could be synthesized in good to high yields in a stepwise manner via iminophosphanes using nitrilium triflates. Symmetrically substituted derivatives could even be obtained in a one-pot procedure from primary phosphanes and nitrilium triflates. Coordination experiments revealed a lability for one of the imine groups, as evidenced by the reaction with $[RhCl(COD)]_2$ that resulted in expulsion of an imidoyl

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chloride with formation of a dinuclear iminophosphane Rh complex. Reaction of *C*-methyl nitrilium triflates with bulky primary phosphanes resulted in a unique 1,3,5-phosphadiazapentadiene that formed a P-coordinated AuCl complex. The bis(imino)phosphanes could be oxidized in high yield with aqueous hydrogen peroxide to the stable corresponding phosphane oxides.

EXPERIMENTAL SECTION

Computational Procedure. Density functional calculations were performed at the ωB97X-D[19] level of theory using Gaussian09, revision D.01.[20] Geometry optimizations were performed using the 6-31+G(d,p)[21] basis set, and the nature of each stationary point was confirmed by frequency calculations.

Preparation of Compounds. All experiments were performed under an atmosphere of dry nitrogen using standard Schlenk-line and glovebox techniques except for the amide syntheses. NMR spectra were recorded at 300 K on a Bruker Advance 250 (^{1}H, ^{13}C, ^{31}P; 85% H_3PO_4), a Bruker Advance 400 (^{1}H, ^{13}C, ^{31}P; 85% H_3PO_4), or a Bruker Advance 500 (^{1}H, ^{13}C) and referenced internally to residual solvent resonances (for $CDCl_3$, ^{1}H at δ 7.26, $^{13}C\{^1H\}$ at δ 77.16; for DMSO-d_6, ^{1}H at δ 2.50, $^{13}C\{^1H\}$ at δ 39.52). Melting points were measured on samples in sealed capillaries on a Buchi M-565 melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer. Electrospray ionization (ESI) mass spectrometry was carried out using a Bruker micrOTOF-Q instrument in positive ion mode (capillary potential of 4500 V). Solvents were distilled from the appropriate drying agents—CaH_2 (DCM), $LiAlH_4$ (pentane), Na (toluene), NaK/benzophenone (diethyl ether, triethylamine), P_2O_5 ($CDCl_3$)—and kept under an inert atmosphere of dry nitrogen. Imidoyl chlorides, nitrilium triflates **1a,b**, and iminophosphane **3a** were obtained according to our previously reported procedure.[12a]

***N*-(2,6-Diisopropylphenyl)pivalamide.**[22] A solution of pivaloyl chloride (12.4 g, 12.7 mL, 103.0 mmol) in THF (50 mL) was added dropwise to a solution of 2,6-diisopropylaniline (17.7 g, 18.9 mL, 100.0 mmol) and triethylamine (10.7 g, 14.8 mL, 106.0 mmol) in THF (200 mL) at 0 °C, after which the reaction mixture was allowed to warm to room temperature and stirred for an additional 4.5 h, after which the resulting suspension was filtered. The filtrate was evaporated to dryness and washed with pentane (3 × 50 mL). The product was obtained as a colorless powder (12.8 g, 49 mmol, 49%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.27 (t, ^3J(H,H) = 7.7 Hz, 1H; *p*-Ar*H*), 7.16 (d, ^3J(H,H) = 7.7 Hz, 2H; *m*-Ar*H*), 6.81 (br s, 1H; N*H*), 3.01 (sept, ^3J(H,H) = 6.9 Hz, 2H; C*H*$(CH_3)_2$), 1.36 (s, 9H; C$(CH_3)_3$), 1.20 (d, ^3J(H,H) = 6.9 Hz, 12H; CH$(CH_3)_2$). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ 177.4 (s; C═O), 146.3 (s; *o*-ArC), 131.0 (s; *ipso*-ArC), 128.2 (s; *p*-ArC), 123.4 (s; *m*-ArC), 45.9 (s; C$(CH_3)_3$), 28.7 (s; CH$(CH_3)_2$), 27.9 (s; C$(CH_3)_3$), 23.6 (s; CH$(CH_3)_2$).

***N*-(2,4,6-Trimethylphenyl)acetamides.**[23] 2,4,6-Trimethylaniline (13.5 g, 14.1 mL, 100.0 mmol) was added dropwise to acetic anhydride (40.8 g, 37.6 mL, 400.0 mmol) in 30 min at 0 °C. Additional acetic anhydride (10 mL) was added to enhance stirring of the reaction mixture. The resulting suspension was stirred for an additional 2 h at room temperature, after which it was filtered. The residue was washed with pentane (3 × 50 mL) to afford the product a colorless powder (18.1 g, 100.0 mmol, 100%). ^{1}H NMR (250.1 MHz, DMSO-d_6): δ 9.01 (br s, 1H; N*H*), 6.85 (s, 2H; *m*-Ar*H*), 2.21 (s, 3H; *p*-ArCH_3), 2.08 (s, 6H; *o*-ArCH_3), 2.01 (s, 3H; CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 168.7 (s; C═O), 137.1 (s; *p*-ArC), 135.3 (s; *o*-ArC), 131.3 (s; *ipso*-ArC), 128.9 (s; *m*-ArC), 23.1 (s; CH_3), 20.9 (s; *p*-ArCH_3), 18.3 (s; *o*-ArCH_3).

***N*-(2,6-Diisopropylphenyl)pivalimidoyl Chloride.**[24] *N*-(2,6-Diisopropylphenyl)pivalamide (10.5 g, 40.0 mmol) was dissolved in thionyl chloride (19.0 g, 11.3 mL, 160 mmol), and the resulting reaction mixture was heated at 70 °C for 2.5 h, which resulted in the evolution of HCl and SO_2 gas, which was neutralized using an aqueous KOH scrubber. The reaction mixture was cooled to room temperature, after which the remaining thionyl chloride was removed *in vacuo* to give a yellow oil (11.0 g, 39.0 mmol, 98%). ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 7.23 (m, 3H; Ar*H*), 2.85 (sept, ^3J(H,H) = 6.6 Hz, 2H; C*H*$(CH_3)_2$), 1.52 (s, 9H; C$(CH_3)_3$), 1.32 (d, ^3J(H,H) = 6.3 Hz, 6H; CH$(CH_3)_2$), 1.26 (d, ^3J(H,H) = 6.3 Hz, 6H; CH$(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 154.7 (s; C═N), 143.3 (s; *ipso*-ArC), 136.5 (s; *o*-ArC), 124.6 (s; *p*-ArCH), 123.0 (s; *m*-ArCH), 44.0 (s; C$(CH_3)_3$), 28.5 (s; CH$(CH_3)_2$), 28.5 (s; C$(CH_3)_3$), 23.2 (s; CH$(CH_3)_2$), 23.0 (s; CH$(CH_3)_2$).

***N*-(2,4,6-Trimethylphenyl)acetimidoyl Chloride.**[25] A solution of oxalyl chloride (6.4 g, 4.3 mL, 50.0 mmol) in DCM (25 mL) was added dropwise to a solution of 2,6-lutidine (8.6 g, 9.3 mL, 80.0 mmol) and *N*-mesitylacetamide (8.9 g, 50.0 mmol) in DCM (150 mL) at 0 °C, to give an orange solution. The solution was kept at 0 °C for 30 min, after which it was stirred for 45 min at room temperature, during which the color turned brown. Volatiles were removed under reduced pressure, and the resulting crude product was extracted into pentane (3 × 40 mL). Extracts were evaporated to dryness, and again an extraction with pentane (15 mL) was performed to remove most of the 2,6-lutidinium chloride. Removal of the solvent yielded a brown oil, which was purified by high-vacuum distillation (2.5×10^{-4} mbar, 60 °C) to give the imidoyl chloride as a light yellow oil (6.6 g, 34.0 mmol, 67%). After distillation the product was kept at −20 °C to prevent decomposition. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 6.88 (s, 2H; *m*-Ar*H*), 2.62 (s, 3H; CH_3), 2.29 (s, 3H; *p*-ArCH_3), 2.06 (s, 6H; *o*-ArCH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 143.3 (s; *p*-ArC), 133.7 (s; *o*-ArC), 128.6 (s; *m*-ArC), 126.4 (s; *ipso*-ArC), 29.2 (s; CH_3), 20.9 (s; *p*-ArCH_3), 17.8 (s; *o*-ArCH_3), unresolved (N═C).

(*N*-(2,6-Diisopropylphenyl))(*tert*-butyl)carbonitrilium Triflate (1c). Trimethylsilyl triflate (11.3 g, 9.2 mL, 50.0 mmol) was added dropwise to a solution of *N*-(2,6-diisopropylphenyl)pivalimidoyl chloride (11.0 g, 40 mmol) in DCM (50 mL) at −78 °C. The resulting suspension was allowed to warm to room temperature and stirred for 30 min, during which the suspended particles dissolved. After 3 h, the solvent was removed *in vacuo* to give a yellow powder, which was purified by slow diffusion of pentane in a concentrated DCM solution to afford **1c** as yellow crystals (10.7 g, 27.0 mmol, 70%). Mp: 122.3 °C (dec). ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 7.58 (t, ^3J(H,H) = 7.9 Hz, 1H; *p*-Ar*H*), 7.29 (d, ^3J(H,H) = 7.9 Hz, 2H; *o*-Ar*H*), 3.16 (sept, ^3J(H,H) = 6.9 Hz, 2H; C*H*$(CH_3)_2$), 1.83 (s, 9H; C$(CH_3)_3$), 1.29 (d, ^3J(H,H) = 6.9 Hz, 12H; CH$(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 147.8 (s; *o*-ArC), 134.3 (s; *p*-ArC), 125.6 (t, ^1J(C,N) = 42.7 Hz; N≡C), 124.5 (s; *m*-ArC), 120.6 (q, ^1J(C,F) = 320.6 Hz; CF_3), 118.3 (t, ^1J(C,N) = 13.1 Hz; *ipso*-ArC), 31.9 (s; C$(CH_3)_3$), 30.0 (s; CH$(CH_3)_2$), 26.8 (s; C$(CH_3)_3$), 22.4 (s; CH$(CH_3)_2$). IR: 2970 (w), 2939 (w), 2878 (w), 2341 (w), 1632 (w), 1585 (w), 1477 (w), 1454 (m), 1389 (w), 1373 (w), 1265 (s), 1223 (s), 1184 (m), 1153 (s), 1138 (s), 1111 (m), 1065 (w), 1030 (s), 937 (w), 879 (w), 806 (m), 752 (m), 633 (s), 571 (m), 517 (m), 463 (w), 436 (w), 424 (w). HR ESI-MS: calcd for $C_{17}H_{26}N$ (M − O_3SCF_3) 244.2060, found 244.2069. *m*/*z* (%): 242.2 (8) $[M - H_2 - O_3SCF_3]^+$, 244.2 (6) $[M - O_3SCF_3]^+$.

(*N*-(2,4,6-Trimethylphenyl))(methyl)carbonitrilium Triflate (1e). Trimethylsilyl triflate (8.0 g, 6.5 mL, 36.0 mmol) was added dropwise to a solution of *N*-(2,4,6-trimethylphenyl)acetimidoyl chloride (6.4 g, 33.0 mmol) in DCM (30 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and was then stirred for 4 h, after which all volatiles were removed *in vacuo*. The resulting yellow solid was washed with pentane (3 × 20 mL) to yield a yellow powder, which was purified by slow diffusion of pentane into a concentrated DCM solution at room temperature to afford **1e** as yellow crystals (6.7 g, 22.0 mmol, 66%). Mp: 137.5−138.1 °C. ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 6.97 (s, 2H; *m*-Ar*H*), 3.42 (s, 3H; CH_3), 2.44 (s, 6H; *o*-ArCH_3), 2.33 (s, 3H; *p*-ArCH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 144.6 (s; *p*-ArC), 138.1 (s; *o*-ArC), 129.7 (s; *m*-ArC), 120.9 (t, ^1J(C,N) = 47.6 Hz; N≡C), 120.7 (q, ^1J(C,F) = 320.6 Hz; CF_3), 118.4 (t, ^1J(C,N) = 14.1 Hz; *ipso*-ArC), 21.7 (s; *p*-ArCH_3), 18.2 (s; *o*-ArCH_3), 5.73 (CH_3). IR: 3136 (w), 3051 (w), 2986 (w), 2928 (w), 2862 (w), 2503 (br w), 2372 (w), 2338 (w), 1670 (w), 1605 (w), 1551 (w), 1481 (w), 1384 (m), 1358 (w), 1292 (m), 1258

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(s), 1223 (s), 1204 (s), 1153 (s), 1023 (s), 953 (w), 933 (w), 864 (m), 818 (w), 756 (w), 710 (w), 636 (s), 598 (m), 571 (m), 555 (w), 517 (s), 451 (w), 432 (w), 405 (w). HR ESI-MS: calcd for $C_{11}H_{14}N$ (M − O_3SCF_3) 160.1121, found 160.1121. *m/z* (%): 160.1 (6) [M − O_3SCF_3]$^+$, 178.1 (20) [M + H_2O − O_3SCF_3]$^+$, 337.2 (100) [M_2 + H + O − $2O_3SCF_3$]$^+$.

***N*-(2,2-Dimethyl-1-(phenylphosphino)propylidene)-2,4,6-trimethylaniline (3b).** Phenylphosphine (3.2 mL of a 0.63 M solution in hexanes, 2.1 mmol) was slowly added to a solution of (*N*-mesityl)(*tert*-butyl)carbonitrilium triflate (**1b**) (0.63 g, 1.8 mmol) in DCM (10 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 1 h to afford protonated intermediate **2b** (δ ^{31}P: −46.5 ppm (d, ^1J(P,H) = 263.6 Hz)). All volatiles were removed *in vacuo*, and the residue was washed with pentane (3 × 10 mL), after which it was dissolved in DCM (10 mL). Then triethylamine (0.30 g, 0.42 mL, 3.0 mmol) was added at room temperature, after which the reaction mixture was stirred for 60 min and the volatiles were removed *in vacuo*. The product was extracted into diethyl ether (3 × 10 mL), after which the extracts were filtered over neutral alumina and evaporated to dryness. **3b** was obtained as a yellow oil (0.56 g, 1.8 mmol, 100%). ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 7.23−7.18 (m, 1H; *p*-PhH), 7.11−7.05 (m, 4H; *o*- and *m*-PhH), 6.84 (s, 1H; *m*-ArH), 6.44 (s, 1H; *m*-ArH), 5.05 (d, ^1J(H,P) = 235.3 Hz, 1H; PH), 2.24 (s, 3H; *p*-ArCH_3), 2.15 (s, 3H; *o*-ArCH_3), 1.45 (s, 3H; *o*-ArCH_3), 1.36 (s, 9H; C(CH_3)$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 183.5 (N═C), 146.3 (d, ^3J(C,P) = 8.2 Hz; *ipso*-ArC), 136.7 (d, ^2J(C,P) = 18.2 Hz; *o*-PhC), 132.5 (s; *p*-ArC), 129.6 (d, ^1J(C,P) = 9.1 Hz; *ipso*-PhC), 129.0 (s; *m*-ArC), 128.8 (s; *p*-PhC), 128.5 (s; *m*-ArC), 128.0 (d, ^3J(C,P) = 8.2 Hz; *m*-PhC), 127.3 (s; *o*-ArC), 123.6 (s; *o*-ArC), 44.2 (d, ^2J(C,P) = 11.8 Hz; C(CH$_3$)$_3$), 29.0 (d, ^3J(C,P) = 3.6 Hz; C(CH_3)$_3$), 20.9 (s; *p*-ArCH_3), 18.2 (d, ^5J(C,P) = 8.7 Hz; *o*-ArCH_3), 17.5 (d, ^5J(C,P) = 2.7 Hz; *o*-ArCH_3). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ −59.7 (d, ^1J(P,H) = 235.3 Hz). IR: 3063 (w), 2962 (m), 2978 (w), 2897 (w), 2862 (w), 2330 (w), 1597 (m), 1531 (w), 1477 (w), 1462 (w), 1447 (w), 1435 (m), 1389 (w), 1331 (w), 1304 (w), 1258 (m), 1231 (w), 1200 (w), 1169 (w), 1092 (m), 1068 (m), 1041 (m), 1022 (s), 980 (m), 937 (w), 923 (w), 903 (m), 868 (w), 841 (m), 798 (s), 756 (s), 729 (s), 690 (s), 636 (w), 609 (m), 575 (m0, 509 (m), 486 (w), 459 (m), 432 (w). HR ESI-MS: calcd for $C_{15}H_{27}NP$ (M + H) 312.1835, found 312.1844. *m/z* (%): 312.2 (25%) [M + H]$^+$.

***N*-(2,2-Dimethyl-1-(phenylphosphino)propylidene)-2,6-diisopropylaniline (3c).** Phenylphosphine (3.2 mL of a 0.63 M solution in hexanes, 2.1 mmol) was added to a solution of (*N*-(2,6-diisopropylphenyl))(*tert*-butyl)carbonitrilium triflate (**1c**; 0.71 g, 1.8 mmol) in DCM (10 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 0.5 h to afford protonated intermediate **3c** (δ ^{31}P: −43.7 ppm (d, ^1J(P,H) = 271.5 Hz)). All volatiles were removed *in vacuo*, and the residue was washed with pentane (3 × 5 mL), after which it was dissolved in DCM (10 mL). Then triethylamine (0.30 g, 0.42 mL, 3.0 mmol) was added at room temperature, after which the reaction mixture was stirred for 60 min and the volatiles were removed *in vacuo*. The product was extracted into diethyl ether (3 × 10 mL), after which the extracts were filtered over neutral alumina and evaporated to dryness to afford **3c** as a yellow oil (0.57 g, 1.6 mmol, 88%). ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 7.23−7.17 (m, 1H; *p*-PhH), 7.15−7.09 (m, 5H; *m*-ArH, *o*- and *m*-PhH), 6.98 (t, ^3J(H,H) = 7.7 Hz, 1H; *p*-ArH), 6.79 (d, ^3J(H,H) = 7.7 Hz, 1H; *m*-ArH), 4.97 (d, ^1J(H,P) = 238.6 Hz, 1H; PH), 2.97 (sept, ^3J(H,H) = 6.8 Hz, 1H; CH(CH$_3$)$_2$), 2.26 (sept, ^3J(H,H) = 7.0 Hz, 1H; CH(CH$_3$)$_2$), 1.38 (d, ^3J(H,H) = 7.0 Hz, 3H; CH(CH_3)$_2$), 1.33 (s, 9H; C(CH_3)$_3$), 1.09 (d, ^3J(H,H) = 6.8 Hz, 3H; CH(CH_3)$_2$), 1.01 (d, ^3J(H,H) = 6.8 Hz, 3H; CH(CH_3)$_2$), 0.85 (d, ^3J(H,H) = 7.0 Hz, 3H; CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 181.3 (N═C), 147.0 (s; *ipso*-ArC), 136.8 (d, ^2J(C,P) = 18.2 Hz; *o*-PhC), 136.2 (s; *o*-ArC), 133.6 (s; *o*-ArC), 130.0 (d, ^1J(C,P) = 10.0 Hz; *ipso*-PhC), 128.8 (s; *p*-PhC), 128.2 (d, ^3J(C,P) = 7.3 Hz; *m*-PhC), 123.5 (s; *p*-ArC), 123.0 (s; *m*-ArC), 122.4 (s; *m*-ArC), 44.5 (d, ^2J(C,P) = 14.5 Hz; C(CH$_3$)$_3$), 29.0 (d, ^3J(C,P) = 3.6 Hz; C(CH_3)$_3$), 28.5 (d, ^5J(C,P) = 1.8 Hz; CH(CH$_3$)$_2$), 28.4 (d, ^5J(C,P) = 4.5 Hz; CH(CH$_3$)$_2$), 23.6 (s; CH(CH_3)$_2$), 23.2 (s; CH(CH_3)$_2$), 21.6 (d, ^6J(C,P) = 1.8 Hz; CH(CH_3)$_2$), 21.1 (d, ^6J(C,P) = 1.8 Hz; CH(CH_3)$_2$). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ −60.0 (d, ^1J(P,H) = 237.8 Hz). IR: 3059 (w), 2959 (s), 2928 (m), 2905 (w), 2866 (m), 2330 (w), 1609 (s), 1585 (m), 1462 (m), 1431 (m), 1381 (w), 1362 (m), 1327 (w), 1304 (w), 1254 (m), 1219 (w), 1180 (w), 1161 (w), 1142 (w), 1111 (w), 1095 (w), 1061 (w), 1038 (m), 984 (m), 933 (m), 903 (m), 837 (m), 806 (m), 795 (m), 756 (s), 737 (s), 698 (s), 640 (w), 621 (w), 602 (w), 586 (w), 536 (w), 501 (w), 459 (m). HR ESI-MS: calcd for $C_{23}H_{33}NP$ (M + H) 354.2345, found 354.2340. *m/z* (%): 354.2 (100%) [M + H]$^+$.

***N,N′*-((Phenylphosphinediyl)bis(2,2-dimethylpropan-1-yl-1-ylidene))dianiline (5a).** *One-Pot Synthesis.* One equivalent of phenylphosphine (0.63 M in hexanes, 0.22 g, 3.2 mL, 2.0 mmol) was added to a solution of 2.5 equiv of (*N*-phenyl)(*tert*-butyl)-carbonitrilium triflate (**1a**; 1.6 g, 5.0 mmol) in DCM (20 mL) at −78 °C. The resulting yellow suspension was kept at −78 °C for 15 min, after which 3 equiv of triethylamine (0.61 g, 0.84 mL, 6.0 mmol) was added. The reaction mixture was stirred for 15 min, after which it was allowed to warm to room temperature and stirred for an additional hour. All volatiles were removed *in vacuo*, and the crude product was extracted into Et_2O (3 × 10 mL), concentrated, and filtered over anhydrous Al_2O_3. Removal of the solvent yielded a yellow powder, which was purified by crystallization from pentane at −20 °C to yield the desired bis(imino)phosphane **5a** as yellow crystals (0.67 g, 1.6 mmol, 78%). Crystals suitable for X-ray analysis were obtained likewise. ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 7.31 (t, ^3J(H,H) = 7.9 Hz, 2H; *o*-PPhH), 7.20−7.11 (m, 5H; *p*-PPhH and *m*-NPhH), 7.09 (t, ^3J(H,H) = 7.3 Hz, 2H; *m*-PPhH), 6.87 (t, ^3J(H,H) = 6.9 Hz, 2H; *p*-NPhH), 6.61 (d, ^3J(H,H) = 6.3 Hz, 4H; *o*-NPhH), 1.12 (s, 18H; C(CH_3)$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.0 (s).

***N,N′*-((Phenylphosphinediyl)bis(2,2-dimethylpropan-1-yl-1-ylidene))bis(2,4,6-trimethylaniline) (5b).** *Stepwise Synthesis.* A solution of iminophosphane **3b** (0.44 g, 1.4 mmol) in DCM (5 mL) was added to a solution of (*N*-mesityl)(*tert*-butyl)carbonitrilium triflate (**1b**; 0.55 g, 1.6 mmol) in DCM (5 mL) at −78 °C, which afforded a yellow suspension. The reaction mixture was allowed to warm to room temperature and stirred for 15 min, giving the protonated intermediate **4b** (^{31}P NMR: − 36.1 ppm (s)), after which triethylamine (0.26 mL, 0.19 g, 1.9 mmol) was added to give an orange solution. After stirring for 1 h, all volatiles were removed *in vacuo*. The product was extracted into Et_2O (4 × 5 mL), after which the combined ether fractions were filtered over neutral alumina and evaporated to dryness to give a yellow powder, which was purified by crystallization from pentane at −20 °C to afford **5b** as yellow crystals (0.54 g, 0.60 mmol, 73%).

One-Pot Synthesis. One equivalent of phenylphosphine (12.7 mL of 0.63 M solution in hexanes, 8.0 mmol) was added to a solution of 2.5 equiv of (*N*-mesityl)(*tert*-butyl)carbonitrilium triflate (**1b**; 7.03 g, 20.0 mmol) in DCM (60 mL) at −78 °C, after which the reaction mixture was stirred for 60 min. Three equivalents of triethylamine (3.4 mL, 2.4 g, 24.0 mmol) was added, and the reaction mixture was stirred for 30 min to give a yellow suspension, which was warmed to room temperature to give a yellow solution. All volatiles were removed *in vacuo*, giving a yellow oil, which was extracted into Et_2O (3 × 10 mL), after which the combined ether fractions were filtered over neutral alumina and evaporated to dryness. The product was purified by crystallization from pentane at −20 °C to afford **5b** as yellow crystals (2.55 g, 5.0 mmol). The mother liquor was evaporated *in vacuo* and crystallized similarly to give **5b** as yellow crystals (1.32 g, 2.5 mmol). Yield: 3.87 g (7.5 mmol, 94%). Mp: 114−120.8 °C. ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 7.71 (t, ^3J(H,H) = 7.8 Hz, 2H; *o*-PhH), 7.26 (t, ^3J(H,H) = 7.4 Hz, 1H; *p*-PhH), 7.19 (t, ^3J(H,H) = 7.5 Hz, 2H; *m*-PhH), 6.67 (s, 2H; *m*-ArH), 6.61 (s, 2H; *m*-ArH), 2.20 (s, 6H; *p*-ArCH_3), 1.98 (s, 6H; *o*-ArCH_3), 1.69 (s, 6H; *o*-ArCH_3), 1.13 (s, 18H; C(CH_3)$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 180.6 (d, ^1J(C,P) = 29.5 Hz; N═C), 147.5 (d, ^3J(C,P) = 5.7 Hz; *ipso*-ArC), 136.8 (d, ^2J(C,P) = 22.9 Hz; *o*-PhC), 135.5 (d, ^1J(C,P) = 10.5 Hz; *ipso*-PhC), 130.3 (s; *p*-ArC), 129.0 (d, ^4J(C,P) = 1.9 Hz; *p*-PhC), 128.3 (s; *m*-ArC), 128.1 (s; *m*-ArC), 127.5 (d, ^3J(C,P) = 127.5 Hz; *m*-PhC), 122.7 (s; *o*-ArC), 122.6 (s; *o*-ArC), 46.1 (d, ^2J(C,P) = 30.5 Hz; C(CH$_3$)$_3$),

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28.9 (d, ^3J(C,P) = 8.8 Hz; C(CH_3)$_3$), 20.7 (s; *p*-ArCH_3), 19.0 (s; *o*-ArCH_3), 19.0 (s; *o*-ArCH_3). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 11.8 (s). IR: 2959 (m), 2920 (m), 2905 (m), 2862 (w), 1651 (m), 1609 (s), 1470 (s), 1431 (m), 1393 (m), 1358 (m), 1304 (w), 1261 (w), 1211 (m), 1192 (m), 1138 (m), 1092 (w), 1065 (w), 1034 (m), 933 (s), 918 (s), 852 (m), 814 (m), 737 (s), 694 (s), 671 (w), 660 (w), 629 (w), 579 (w), 555 (w), 517 (m), 505 (w), 482 (w), 455 (m), 420 (w). HR ESI-MS: calcd for $C_{34}H_{46}N_2P$ (M + H) 513.3393, found 513.3347. *m*/*z* (%): 202.2 (100%) [**1b** − O_3SCF_3]$^+$, 513.3 (4%) [M + H]$^+$.

***N,N′*-((Phenylphosphinediyl)bis(2,2-dimethylpropan-1-yl-1-ylidene))bis(2,6-diisopropylaniline) (5c).** *Stepwise Synthesis.* A solution of iminophosphane **3c** (0.44 g, 1.3 mmol) in DCM (2.5 mL) was added to a solution of (*N*-(2,6-diisopropylphenyl))(*tert*-butyl)-carbonitrilium triflate (**1c**; 0.54 g, 1.4 mmol) in DCM (2.5 mL) at −78 °C, which afforded a yellow suspension. The reaction mixture was allowed to warm to room temperature and stirred for 15 min, giving the protonated intermediate **4c** (δ ^{31}P: −43.5 ppm (d, ^1J(P,H) = 269.5 Hz, major) and −8.3 ppm (s, minor)), after which triethylamine (0.23 mL, 0.16 g, 1.9 mmol) was added to give an orange solution, which was stirred for 1.5 h. ^{31}P NMR spectroscopy showed that **3c** was still present; therefore, a solution of nitrilium triflate **1c** (0.16 g, 0.40 mmol) in DCM (2.5 mL) was added at −78 °C, and stirring was continued for 30 min, after which triethylamine was added (0.05 mL, 0.03 g, 0.40 mmol). After stirring for 30 min at room temperature, the volatiles were removed *in vacuo*. Solid (*N*-(2,6-diisopropylphenyl))-(*tert*-butyl)carbonitrilium triflate (**1c**; 0.03 g, 0.09 mmol) was added, and the mixture was dissolved in DCM (10 mL), after which triethylamine (0.007 g, 0.009 mL, 0.09 mmol) was added. The reaction mixture was stirred for 30 min, after which the solvent was removed under reduced pressure. The product was extracted into Et_2O (4 × 5 mL), after which the combined etheral fractions were filtered over neutral alumina and evaporated to dryness to obtain a yellow powder, which was crystallized from pentane at −20 °C to afford **5c** as yellow crystals (0.31 g, 0.52 mmol, 42%).

One-Pot Synthesis. One equivalent of phenylphosphine (3.2 mL of a 0.63 M solution in hexanes, 2.0 mmol) was slowly added to a solution of 2.5 equiv of (*N*-(2,6-diisopropylphenyl))(*tert*-butyl)-carbonitrilium triflate (**1c**; 2.0 g, 5.0 mmol) in DCM (20 mL) at −78 °C. The resulting solution was stirred for 60 min at the same temperature, after which 3 equiv of triethylamine (0.84 mL, 0.61 g, 6.0 mmol) was added. The reaction mixture was kept at −78 °C for 30 min and was then warmed to room temperature over the course of 1 h. All volatiles were removed *in vacuo*, and the resulting product was extracted into diethyl ether (5 × 10 mL). The combined etheral fractions were concentrated, filtered over neutral alumina, and then evaporated to dryness. The product was purified by crystallization from pentane at −20 °C to give **5c** as yellow crystals (0.85 g, 1.4 mmol, 71%). Mp: 104.6−114.2 °C. ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 7.66 (t, ^3J(H,H) = 7.9 Hz, 2H; *o*-PhH), 7.26−7.20 (m, 1H; *p*-PhH), 7.17 (t, ^3J(H,H) = 7.3 Hz, 2H; *m*-PhH), 6.96−6.85 (m, 6H; *m*- and *p*-ArH), 2.82 (sept, ^3J(H,H) = 6.6 Hz; 2H; CH(CH_3)$_2$), 2.41 (sept, ^3J(H,H) = 6.6 Hz; 2H; CH(CH_3)$_2$), 1.21 (s, 18H; C(CH_3)$_3$), 1.13 (d, ^3J(H,H) = 6.7 Hz; 6H; CH(CH_3)$_2$), 1.01 (d, ^3J(H,H) = 6.7 Hz; 6H; CH(CH_3)$_2$), 0.97 (d, ^3J(H,H) = 6.3 Hz; 6H; CH(CH_3)$_2$), 0.73 (d, ^3J(H,H) = 6.3 Hz; 6H; CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 179.6 (N=*C*), 147.1 (d, ^3J(C,P) = 6.4 Hz; *ipso*-ArC), 137.4 (d, ^2J(C,P) = 24.5 Hz; *o*-PhC), 134.0 (d, ^1J(C,P) = 7.3 Hz; *ipso*-PhC), 133.7 (s; *o*-ArC), 133.2 (s; *o*-ArC), 129.4 (s; *p*-PhC), 127.4 (d, ^3J(C,P) = 9.8 Hz; *m*-PhC), 122.4 (s; *m*-ArC), 122.3 (s; *m*-ArC), 122.2 (s; *p*-ArC), 46.7 (*C*(CH$_3$)$_3$), 29.3 (d, ^3J(C,P) = 7.7 Hz; C(*C*H$_3$)$_3$), 28.3 (s; CH(*C*H$_3$)$_2$), 28.0 (s; CH(*C*H$_3$)$_2$), 24.2 (s; CH(*C*H$_3$)$_2$), 24.0 (s; CH(*C*H$_3$)$_2$), 22.7 (s; CH(*C*H$_3$)$_2$), 22.4 (s; CH(*C*H$_3$)$_2$). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 10.8 (s). IR: 2959 (s), 2932 (m), 2905 (w), 2866 (m), 1632 (m), 1616 (m), 1589 (w), 1458 (m), 1423 (m), 1381 (m), 1358 (m), 1323 (w), 1258 (m), 1196 (w), 1180 (w), 1157 (w), 1088 (m), 1034 (m), 953 (w), 930 (m), 906 (s), 806 (m), 741 (s), 702 (m), 694 (m), 667 (w), 644 (w), 621 (w), 579 (m), 517 (w), 501 (w), 486 (w), 467 (s), 444 (s). HR ESI-MS: calcd for $C_{23}H_{33}NP$ (M − Dipp-N≡C-*t*Bu + 2H) 354.2345, found 354.2400. *m*/*z* (%): 244.2 (9) [Dipp-N≡C-*t*Bu]$^+$, 262.2 (44) [Dipp-N≡C-*t*Bu + H_2O]$^+$, 354.2 (100) [M − Dipp-N≡C-*t*Bu + 2H]$^+$.

***N*-(1-((−2,2-Dimethyl-1-(phenylimino)propyl)(phenyl)-phosphino)-2,2-dimethylpropylidene)-2,4,6-trimethylaniline (5d).** A solution of iminophosphane **3a** (0.32 g, 1.2 mmol) in DCM (5 mL) was added to a solution of (*N*-mesityl)(*tert*-butyl)carbonitrilium triflate (**1b**; 0.46 g, 1.3 mmol) in DCM (5 mL) at −78 °C, which afforded a yellow suspension. The mixture was allowed to warm to room temperature and stirred for 15 min, yielding the protonated intermediate **4d** (δ ^{31}P: 40.2 ppm (s)). Next, triethylamine (0.21 mL, 0.16 g 1.5 mmol) was added, and the yellow reaction mixture was stirred for 1 h, after which all volatiles were removed *in vacuo*. The product was extracted into Et_2O (3 × 10 mL), after which the combined etheral fractions were filtered over neutral alumina and evaporated to dryness. The yellow powder was crystallized from pentane at 6 °C to afford **5d** as yellow crystals (0.31 g, 0.66 mmol, 55%). Crystals suitable for X-ray analysis were obtained accordingly. Mp: 102.8−120.8 °C. ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 7.46 (t, ^3J(H,H) = 8.3 Hz, 2H; *o*-PPhH), 7.29 (t, ^3J(H,H) = 7.8 Hz, 2H; *m*-NPhH), 7.16−7.11 (m, 1H; *p*-PPhH), 7.01 (t, ^3J(H,H) = 7.4 Hz, 2H; *m*-PPhH), 6.97 (t, ^3J(H,H) = 7.8 Hz, 1H; *p*-NPhH), 6.76 (d, ^3J(H,H) = 7.9 Hz, 2H; *o*-NPhH), 6.54 (s, 1H; *m*-ArH), 6.09 (s, 1H; *m*-ArH), 2.07 (s, 3H; *o*-ArCH_3), 2.03 (s, 3H; *p*-ArCH_3), 1.71 (s, 3H; *o*-ArCH_3), 1.39 (s, 9H; Mes-N=C−C(CH_3)$_3$), 0.92 (s, 9H; Ph-N=C−C(CH_3)$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 184.9 (d, ^1J(C,P) = 21.0 Hz; Ph-N=*C*), 177.6 (d, ^1J(C,P) = 55.3 Hz; Mes-N=*C*), 152.2 (d, ^3J(C,P) = 6.7 Hz; *ipso*-NPhC), 145.4 (d, ^3J(C,P) = 5.7 Hz; *ipso*-ArC), 135.4 (d, ^2J(C,P) = 21.9 Hz; *o*-PPhC), 131.8 (d, ^1J(C,P) = 10.5 Hz; *ipso*-PPhC), 130.6 (s; *p*-ArC), 128.6 (s; *m*-NPhC or *p*-PPhC), 128.6 (s; *m*-NPhC or *p*-PPhC), 127.8 (s; *m*-ArC), 127.7 (s; *m*-ArC), 127.5 (d, ^3J(C,P) = 9.5 Hz; *m*-PPhC), 124.1 (s; *o*-ArC), 122.9 (s; *o*-ArC), 121.8 (s; *p*-NPhC), 116.6 (s; *o*-NPhC), 46.1 (d, ^2J(C,P) = 29.6 Hz; Ph-N=C-*C*(CH$_3$)$_3$), 45.1 (d, ^2J(C,P) = 28.6 Hz; Mes-N=C-*C*(CH$_3$)$_3$), 30.6 (d, ^3J(C,P) = 6.7 Hz; Ph-N=C−C(*C*H$_3$)$_3$), 29.7 (d, ^3J(C,P) = 5.7 Hz; Mes-N=C−C(*C*H$_3$)$_3$), 20.6 (s; *p*-ArCH_3), 18.7 (s; *o*-ArCH_3), 18.6 (s; *o*-ArCH_3). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 17.9 (s). IR: 3074 (w), 3055 (w), 2997 (w), 2982 (w), 2959 (m), 2928 (w), 2905 (w), 2866 (w), 2723 (w), 1647 (w), 1620 (s), 1593 (m), 1574 (w), 1516 (w), 1474 (s), 1435 (m), 1393 (w), 1373 (w), 1354 (m), 1304 (w), 1261 (m), 1238 (m), 1215 (w), 1188 (s), 1165 (w), 1146 (w), 1088 (m), 1068 (m), 1022 (s), 945 (s), 923 (m), 891 (w), 872 (w), 849 (m), 795 (s), 756 (s), 737 (s), 690 (s), 671 (m), 656 (m), 629 (m), 586 (w), 563 (w), 521 (w), 505 (m), 486 (m), 459 (w), 436 (w). HR ESI-MS: calcd for $C_{17}H_{21}NP$ (M − Mes-NC-*t*Bu + 2H) 270.1406, found 270.1404; calcd for $C_{20}H_{27}NP$ (M − Ph-NC-*t*Bu + 2H) 312.1876, found 312.1867. *m*/*z* (%): 270.1 (100%) [M − Ph-NC-*t*Bu + 2H]$^+$, 312.2 (84%) [M − Ph-NC-*t*Bu + 2H]$^+$.

Rhodium Complex 6. A mixture of 1 equiv of **5b** (0.100 g, 0.20 mmol) and 1.5 equiv of [RhCl(COD)]$_2$ (0.144 g, 0.29 mmol) was dissolved in DCM (6 mL), which afforded an orange solution, which was stirred for 10 min. Removing all volatiles under reduced pressure gave an orange solid, which was crystallized by slow diffusion of Et_2O into a concentrated DCM solution at 7 °C to give orange crystals, which were recrystallized by slow diffusion of Et_2O into a concentrated DCM solution at room temperature to afford **6** (0.065 g) as orange crystals, which were suitable for X-ray analysis. The mother liquor was evaporated to dryness under reduced pressure and crystallized again under similar conditions to afford **6** (0.100 g) as orange crystals. Yield: 0.165 g (0.19 mmol, 97%). Mp: 187−193 °C (dec). ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 8.57−8.46 (m, 2H; *o*-PhH), 7.39−7.31 (m, 3H; *m*- and *p*-PhH), 6.78 (s, 2H; *m*-ArH), 4.23 (br s, 3H; CODH), 2.55−2.26 (m, 16H; *o*-ArCH_3 and CODH), 2.22 (s, 3H; *p*-ArCH_3), 2.05−1.83 (m, 8H; CODH), 1.80−1.70 (m, 3H; CODH), 0.98 (s, 9H; C(CH_3)$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 143.9 (d, ^3J(C,P) = 10.0 Hz; *ipso*-ArC), 138.3 (d, ^2J(C,P) = 9.1 Hz; *o*-PhC), 135.2 (d, ^1J(C,P) = 4.5 Hz; *ipso*-PhC), 135.0 (s; *p*-ArC), 129.1 (s; *m*-ArC), 128.9 (s; *p*-PhC), 127.6 (d, ^3J(C,P) = 8.2 Hz; *m*-PhC), 127.3 (s; *o*-ArC), 78.9 (d, ^1J(C,Rh) = 13.6 Hz; CODC), 44.8 (s; *C*(CH$_3$)$_3$), 32.9 (s; CODC), 32.6 (br s; CODC), 31.0 (s; CODC), 29.4 (s; CODC), 29.2 (s; CODC), 28.4 (s; C(*C*H$_3$)$_3$), 20.8 (s; *p*-ArCH_3), 19.9 (br s; *o*-

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ArCH$_3$), unresolved (N=C). ^{31}P NMR (162.0 MHz, CDCl$_3$): δ −13.7 (t, ^1J(P,Rh) = 104.0 Hz). IR: 3016 (w), 2932 (m), 2912 (m), 2870 (m), 2824 (m), 1547 (m), 1508 (w), 1470 (m), 1427 (m), 1389 (m), 1377 (w), 1362 (w), 1327 (m), 1304 (w), 1269 (m), 1234 (w), 1211 (w), 1192 (m), 1177 (m), 1153 (w), 1138 (m), 1080 (m), 1045 (w), 1026 (w), 980 (m), 949 (m), 933 (w), 883 (w), 856 (m), 829 (m), 818 (m), 791 (w), 775 (w), 748 (m), 729 (s), 706 (s), 667 (m), 633 (w), 582 (m), 559 (w), 536 (m), 505 (m), 490 (m), 474 (m), 455 (w), 424 (s). HR ESI-MS: calcd for $C_{36}H_{50}ClNPRh_2$ (M + H) 768.1474, found 768.1478. *m*/*z* (%): 312.2 (80) [M − $Rh_2Cl(COD)_2$ + 2H]$^+$, 522.2 (100) [M − RhCl(COD) + H]$^+$, 768.1 (90) [M + H]$^+$.

Reaction between *N*-(Mesityl)pivalimidoyl Chloride and [CODRhCl]$_2$. A solution of *N*-(mesityl)pivalimidoyl chloride (0.10 g, 0.42 mmol) in DCM (2.5 mL) was slowly added to a solution of [RhCl(COD)]$_2$ (0.10 g, 0.21 mmol) in DCM (2.5 mL), after which the reaction mixture was stirred for 1 h. The brown solution was evaporated to dryness under reduced pressure to obtain a pale brown wax (0.20 g; 0.42 mmol, 100%). ^{1}H NMR (500.2 MHz, CDCl$_3$): δ 6.85 (s, 2H; *m*-ArH), 4.23 (br s, 4H; CODH), 2.54−2.45 (m, 4H; CODH), 2.26 (s; *p*-ArCH$_3$), 2.00 (s; *o*-ArCH$_3$), 1.79−1.72 (m, 4H; CODH), 1.41 (s, 9H; C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, CDCl$_3$): δ 155.5 (s; N=C), 143.2 (s; *ipso*-ArC), 133.3 (s; *p*-ArC), 128.6 (s; *m*-ArC), 126.1 (s; *o*-ArC), 78.9 (d, ^1J(C,Rh) = 13.6 Hz; CODC), 44.0 (s; C(CH$_3$)$_3$), 31.0 (s; CODC), 29.7 (s; C(CH$_3$)$_3$), 21.0 (s; *p*-ArCH$_3$), 17.7 (s; *o*-ArCH$_3$). IR: 2988 (w), 2974 (w), 2934 (m), 2910 (m), 2868 (m), 2827 (m), 1697 (m), 1647 (w), 1508 (w), 1475 (m), 1466 (m), 1447 (m), 1423 (w), 1396 (w), 1364 (w), 1323 (m), 1298 (m), 1250 (m), 1227 (w), 1209 (w), 1171 (m), 1150 (m), 1078 (w), 1041 (w), 1034 (w), 993 (m), 959 (s), 935 (m), 866 (m), 851 (m), 814 (s), 773 (m), 795 (m), 735 (w), 689 (w), 609 (m), 592 (w), 579 (m), 565 (w), 538 (w), 513 (w), 486 (s), 473 (m).

2,4,6-Trimethyl-*N*-(1-((2,4,6-tri-*tert*-butylphenyl)-phosphanylidene)ethyl)aniline (7). A solution of supermesityl phosphane (0.70 g, 2.51 mmol) in DCM (8 mL) was added to a solution of nitrilium triflate **1e** (0.79 g, 2.55 mmol) in DCM (8 mL) at −78 °C to give a bright yellow solution of the protonated intermediate (^{31}P NMR: −39.96 (d, ^1J(P,H) = 264.0 Hz), −48.25 (d, ^1J(P,H) = 264.0 Hz)). After stirring the reaction mixture for 15 min at room temperature, triethylamine (0.5 g, 0.7 mL, 5.1 mmol) was added to give a yellow solution, which was stirred for 1 h. The mixture was evaporated to give a yellow solid, which was extracted into Et$_2$O (10 mL + 5 × 5 mL) and filtered over Celite. Crystallization from Et$_2$O at −20 °C afforded a mixture of *Z*-7 and *E*-7, in a ratio of 4:1 according to ^{1}H NMR spectroscopy, as a yellow solid (0.63 g, 1.4 mmol, 57%). Mp: 106 °C. ^{1}H NMR (250.1 MHz, CDCl$_3$, *Z*-7): δ 7.39 (d, ^4J(H,P) = 1.3 Hz, 2H; *m*-Mes*H), 6.76 (s, 2H; *m*-MesH), 4.71 (s, 1H; NH), 2.20 (s, 3H; *p*-MesCH$_3$), 1.97 (s, 6H; *o*-MesCH$_3$), 1.76 (d, ^3J(H,P) = 21.0 Hz, 3H; P=C−CH$_3$), 1.63 (d, ^5J(H,P) = 0.8 Hz, 18H; *o*-Mes*C(CH$_3$)$_3$), 1.28 (s, 9H; *p*-Mes*C(CH$_3$)$_3$). ^{1}H NMR (250.1 MHz, CDCl$_3$, *E*-7): δ 7.40 (s, 2H; *m*-Mes*H), 6.94 (s, 2H; *m*-MesH), 5.45 (s, 1H; NH), 2.33 (s, 6H; *o*-MesCH$_3$), 2.30 (s, 3H; *p*-MesCH$_3$), 1.54 (s, 18H; *o*-Mes*C(CH$_3$)$_3$), 1.32 (s, 9H; *p*-Mes*C(CH$_3$)$_3$), P=C−CH$_3$ is unresolved. ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$, *Z*-7): 179.5 (d, ^1J(C,P) = 65.1 Hz; C=P), 156.2 (s; *o*-Mes*C), 149.1 (s; *p*-Mes*C), 136.1 (s; *o*-MesC), 136.0 (d, ^1J(C,P) = 46.1 Hz; *ipso*-Mes*C), 136.0 (s; *ipso*-MesC), 136.0 (s; *p*-MesC), 129.1 (s; *m*-MesC), 121.5 (s; *m*-Mes*C), 38.6 (s; *o*-Mes*C(CH$_3$)$_3$), 33.3 (d, ^4J(C,P) = 8.1 Hz; *o*-Mes*C(CH$_3$)$_3$), 31.5 (s; *p*-Mes*C(CH$_3$)$_3$), 21.3 (s; P=C-CH$_3$), 20.8 (s; *o*-MesCH$_3$), 19.5 (s; *p*-MesCH$_3$), *p*-Mes*C(CH$_3$)$_3$ is unresolved. ^{31}P NMR (101.3 MHz, CDCl$_3$): δ 65.82 (q, ^3J(P,H) = 20.3 Hz; *Z*-7), 98.10 (q, ^3J(P,H) = 9.6 Hz; *E*-7). IR: 2953 (m), 2907 (w), 2866 (w), 1582 (w), 1479 (m), 1391 (w), 1366 (m), 1358 (m), 1325 (m), 1259 (s), 1217 (m), 1204 (w), 1173 (w), 1150 (m), 1126 (m), 1094 (m), 1028 (s), 970 (w), 928 (w), 903 (w), 878 (m), 862 (m), 802 (s), 609 (w), 596 (w), 579 (w), 542 (w), 517 (m), 494 (w), 459 (m). HR ESI-MS: calcd for $C_{40}H_{58}N_2P$ (M + Mes-N≡C-Me): 597.4332, found 597.4342. *m*/*z* (%): 160.1 (12) [**1e** − O_3SCF_3]$^+$ 351.2 (44) [M + Mes-N≡C-Me − Mes*]$^+$, 438.3 (<1) [M + H]$^+$, 597.4 (100) [M + Mes-N≡C-Me]$^+$.

(*E*)-*N*,*N*′-Dimesityl-*N*-((*E*)-1-((2,4,6-tri-*tert*-butylphenyl)-phosphanylidene)ethyl)acetimidamide (9). *Stepwise NMR-Scale Reaction.* A solution of aminophosphaalkene 7 (0.04 mmol) in DCM (0.6 mL) was added to a NMR tube containing nitrilium triflate **1e** (0.05 mmol) at −78 °C to give a bright yellow solution, which then was warmed to room temperature. The mixture was stirred and the protonated bis(imino)phosphane **4e** was observed by ^{31}P NMR spectroscopy (δ 11.3 ppm). The reaction was monitored using ^{31}P NMR spectroscopy, and after 120 h complete conversion toward P,N,N-intermediate **8** was observed (δ ^{31}P: 174.6 (s)). A solution of triethylamine (0.07 mmol) in DCM (0.2 mL) was added to give a yellow solution, which was stirred for 1 h, giving P,N,N-ligand **9** with full conversion (δ ^{31}P: 186.6 (s)). The product was not isolated.

One-Pot Synthesis. A solution of 2,4,6-tris-*tert*-butylphenyl-phosphane (0.76 g, 2.7 mmol) in DCM (10 mL) was slowly added to a solution of (*N*-(2,4,6-trimethylphenyl))(methyl)carbonitrilium triflate (**1e**; 2.12 g, 6.9 mmol) in DCM (30 mL) at −78 °C. After stirring the reaction mixture at this temperature for 2.5 h, triethylamine (0.8 g, 1.2 mL, 8.2 mmol) was added over a period of 5 min. The reaction mixture was stirred for another 2.5 h at this temperature and then warmed to room temperature. All volatiles were evaporated, and the product was extracted into Et$_2$O (3 × 15 mL), after which the filtrate was filtered over neutral alumina eluting with Et$_2$O. Evaporation of all volatiles gave 1.65 g (2.7 mmol, 100%) of **9** as a yellow solid. Mp: 131.4−134.0 °C. ^{1}H NMR (500.2 MHz, CDCl$_3$): δ 7.35 (s, 2H; *m*-Mes*H), 6.92 (s, 2H; (C$_2$N)-*m*-MesH), 6.87 (s, 2H; (C=N)-*m*-MesH), 2.29 (s, 3H; (C$_2$N)-*p*-MesCH$_3$), 2.26 (s, 3H; (C=N)-*p*-MesCH$_3$), 2.19 (s, 6H; (C$_2$N)-*o*-MesCH$_3$), 2.12 (s, 6H; (C=N)-*o*-MesCH$_3$), 1.55 (s, 18H; *o*-Mes*CH$_3$), 1.41 (s, 3H; N=C-CH$_3$), 1.29 (s, 9H; *p*-Mes*CH$_3$), 1.25 (d, ^3J(H,H) = 9.8 Hz, 3H; P=C-CH$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, CDCl$_3$): δ 181.0 (d, ^1J(C,P) = 65.4 Hz; P=C), 153.8 (d, ^2J(C,P) = 2.7 Hz; *o*-Mes*C), 153.0 (d, ^3J(C,P) = 3.6 Hz; N=C), 148.8 (s; *p*-Mes*C), 144.8 (s; (C=N)-*ipso*-MesC), 142.5 (d, ^1J(C,P) = 72.7 Hz; *ipso*-Mes*C), 139.5 (s; (C$_2$N)-*ipso*-MesC),137.9 (s; (C$_2$N)-*p*-MesC), 136.4 (s; (C$_2$N)-*o*-MesC), 130.8 (s; (N=C)-*p*-MesC), 129.5 (s; (C$_2$N)-*m*-MesC), 128.5 (s; (N=C)-*m*-MesC), 127.4 (s; (N=C)-*o*-MesC), 121.5 (s; *m*-Mes*C), 38.4 (s; *o*-Mes*-C(CH$_3$)$_3$), 35.0 (s; *p*-Mes*-C(CH$_3$)$_3$), 32.8 (d, ^4J(C,P) = 9.1 Hz; *o*-Mes*-C(CH$_3$)$_3$), 31.6 (s; *p*-Mes*-C(CH$_3$)$_3$), 24.5 (d, ^2J(C,P) = 14.5 Hz; P=C-CH$_3$), 21.2 (s; (C$_2$N)-*p*-MesCH$_3$), 20.9 (s; (C=N)-*p*-MesCH$_3$), 18.7 (s; (C=N)-*o*-MesCH$_3$), 18.1 (s; (C$_2$N)-*o*-MesCH$_3$), 17.0 (d, ^4J(C,P) = 3.6 Hz; N=C-CH$_3$). ^{31}P NMR (162.0 MHz, CDCl$_3$): δ 188.9. IR: 2949 (m), 2910 (m), 2862 (w), 1649 (s), 1609 (w), 1593 (w), 1477 (m), 1460 (w), 1408 (w), 1389 (m), 1367 (m), 1360 (m), 1340 (m), 1300 (m), 1273 (s), 1240 (m), 1225 (s), 1194 (m), 1184 (m), 1142 (w), 1128 (m), 1024 (w), 1011 (m), 933 (w), 926 (w), 904 (w), 876 (m), 851 (s), 800 (w), 773 (m), 758 (m), 723 (w), 662 (w), 648 (w), 615 (w), 586 (m), 579 (m), 567 (m), 513 (w), 474 (w). HR ESI-MS: calcd for $C_{40}H_{58}N_2P$ (M + H) 597.4332, found 597.4302. *m*/*z* (%): 351.2 (100) [M − Mes*]$^+$, 597.4 (27) [M + H]$^+$.

(*E*)-*N*,*N*′-Dimesityl-*N*-((*E*)-1-((2,4,6-tri-*tert*-butylphenyl)-phosphanylidene)ethyl)acetimidamide Gold(I) Chloride Complex (10). **9** (55 mg, 0.092 mmol) and dimethylsulfide gold(I) chloride (22 mg, 0.074 mmol) were dissolved in DCM (4 mL) and stirred for 30 min at room temperature. Subsequently, all volatiles were removed *in vacuo*, and the remaining yellow solid was washed with pentane to obtain 20 mg (0.024 mmol, 32%) of **10** as a pale yellow solid. Mp: 93.1 °C (dec). ^{1}H NMR (500.2 MHz, CDCl$_3$): δ 7.51 (d, ^4J(H,P) = 3.5 Hz, 2H; *m*-Mes*H), 7.11 (s, 2H; (C$_2$N)-*m*-MesH), 6.82 (s, 2H; (C=N)-*m*-MesH), 2.43 (s, 3H; (C$_2$N)-*p*-MesCH$_3$), 2.37 (s, 6H; (C$_2$N)-*o*-MesCH$_3$), 2.23 (s; (C=N)-*p*-MesCH$_3$), 2.02 (s, 6H; (C=N)-*o*-MesCH$_3$), 1.99 (d, ^3J(H,P) = 23.3 Hz, 3H; P=C−CH$_3$), 1.65 (s, 18H; *o*-Mes*C(CH$_3$)$_3$), 1.39 (s; N=C−CH$_3$), 1.31 (s, 9H; *p*-Mes*C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, CDCl$_3$): δ 177.2 (d, ^2J(C,P) = 80.8 Hz; P=C), 156.8 (d, ^2J(C,P) = 39.1 Hz; *o*-Mes*C), 154.7 (d, ^3J(C,P) = 4.5 Hz; N=C), 153.5 (d, ^4J(C,P) = 2.3 Hz; *p*-Mes*C), 144.6 (s; (C=N)-*ipso*-MesC), 140.5 (s; (C$_2$N)-*p*-MesC), 137.5 (d, ^3J(C,P) = 6.4 Hz; (C$_2$N)-*ipso*-MesC), 135.7 (d, ^4J(C,P) = 2.7 Hz; (C$_2$N)-*o*-MesC), 132.0 (s; (C=N)-*p*-MesC),

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131.6 (s; (C═N)-*m*-MesCH), 129.0 (s; (C_2N)-*m*-MesCH), 126.8 (s; (C═N)-*o*-MesC), 124.5 (d, ^1J(C,P) = 39.1 Hz; *ipso*-Mes*C), 123.7 (d, ^2J(C,P) = 9.1 Hz; *m*-Mes*CH), 39.4 (s; *o*-Mes*$C(CH_3)_3$), 35.4 (s; *p*-Mes*$C(CH_3)_3$), 34.3 (d, ^4J(C,P) = 1.8 Hz; *o*-Mes*$C(CH_3)_3$), 31.3 (s; *p*-Mes*$C(CH_3)_3$), 25.4 (d, ^2J(C,P) = 1.8 Hz; P═C-CH_3), 21.5 (s; (C═N)-*p*-MesCH_3), 20.7 (s; (C_2N)-*p*-MesCH_3), 18.9 (s; (C_2N)-*o*-MesCH_3), 18.8 (s; (C═N)-*o*-MesCH_3), 17.0 (d, ^4J(C,P) = 3.1 Hz; N═C-CH_3). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 129.4. IR: 2955 (m), 2908 (m), 2868 (w), 1637 (m), 1609 (w), 1593 (m), 1528 (w), 1477 (m), 1445 (m), 1394 (w), 1364 (m), 1288 (s), 1269 (s), 1236 (m), 1211 (s), 1140 (m), 1126 (m), 1011 (m), 972 (w), 951 (w), 930 (w), 879 (m), 852 (m), 814 (w), 804 (w), 783 (w), 754 (m), 735 (m), 719 (w), 650 (w), 623 (m), 608 (w), 594 (w), 577 (m), 567 (m), 542 (w), 525 (w), 469 (w). HR ESI-MS: calcd for $C_{40}H_{58}N_2P$ (M − AuCl + H) 597.4332, found 597.4334. *m*/*z* (%): 295.2 (20) [M − AuCl − Me-CP-Mes* + 2H]$^+$, 351.2 (100) [M − Mes* − AuCl]$^+$, 597.4 (25) [M − AuCl + H]$^+$.

(1-(Mesitylimino)-2,2-dimethylpropyl)(1-(mesitylimino)-2,2-dimethylpropyl)(phenyl)phosphine Oxide (11b). Hydrogen peroxide (1.32 mL of a 11.46 M solution in H_2O, 15.20 mmol) was added to a solution of **5b** (0.77 g, 1.52 mmol) in toluene (15 mL) at 0 °C, after which the reaction mixture was vigorously stirred for 30 min at room temperature. The toluene layer was isolated, and the water layer was extracted with 5 mL of toluene. The combined toluene layers were evaporated to dryness. Crystallization of the remaining yellow solid from a minimal amount of diethyl ether at −20 °C gave two batches of yellow solid with a total yield of 0.63 g (1,19 mmol, 78%). Mp: 202.3−203.7 °C. ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 8.13−8.07 (m, 2H; *o*-PhH), 7.46 (t, ^3J(H,H) = 7.3 Hz, 1H; *p*-PhH), 7.39 (dt, ^4J(H,P) = 2.5 Hz, ^3J(H,H) = 7.5 Hz, 2H; *m*-PhH), 6.73 (s, 2H; *m*-ArH), 6.67 (s, 2H; *m*-ArH), 2.21 (s, 6H; *p*-ArCH_3), 2.01 (s, 6H; *o*-ArCH_3), 1.62 (s, 6H; *o*-ArCH_3), 1.20 (s, 18H; $C(CH_3)_3$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 176.5 (d, ^1J(C,P) = 108.2 Hz; N═C), 146.4 (d, ^3J(C,P) = 26.3 Hz; *ipso*-ArC), 134.5 (d, ^1J(C,P) = 89.9 Hz; *ipso*-PhC), 132.9 (d, ^2J(C,P) = 29.1 Hz; *o*-PhC), 131.3 (s; *p*-ArC), 131.2 (d, ^4J(C,P) = 2.7 Hz; *p*-PhC), 128.4 (s; *m*-ArC), 128.2 (s; *m*-ArC), 127.5 (d, ^3J(C,P) = 11.8 Hz; *m*-PhC), 122.2 (s; *o*-ArC), 122.1 (s; *o*-ArC), 46.7 (d, ^2J(C,P) = 29.1 Hz; $C(CH_3)_3$), 28.4 (d, ^3J(C,P) = 2.2 Hz; $C(CH_3)_3$), 20.7 (s; *p*-ArCH_3), 18.9 (s; *o*-ArCH_3), 18.9 (s; *o*-ArCH_3). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 22.8 (s). IR: 2993 (w), 2970 (w), 2955 (w), 2941 (w), 2908 (w), 2866 (w), 1653 (m), 1630 (m), 1474 (s), 1441 (m), 1394 (w), 1377 (w), 1360 (w), 1310 (w), 1213 (m), 1173 (s), 1138 (m), 1099 (m), 1070 (w), 1047 (m), 1030 (m), 1013 (w), 964 (w), 955 (w), 930 (w), 887 (w), 856 (s), 820 (w), 744 (s), 739 (s), 710 (s), 698 (s), 670 (w), 636 (w), 586 (s), 567 (w), 532 (s), 513 (s), 496 (s), 478 (s). HR ESI-MS: calcd for $C_{20}H_{27}NOP$ (M − Mes-N≡C-*t*Bu + 2H) 328.1825, found 328.1832. *m*/*z* (%): 202.2 (12) [Mes-N≡C-*t*Bu]$^+$, 220.2 (100) [Mes-N≡C-*t*Bu + H_2O]$^+$, 328.2 (24) [M − Mes-N≡C-*t*Bu + 2H]$^+$.

1,1′-(Phenylphosphanediyl)bis(*N*-(2,6-diisopropylphenyl)-2,2-dimethylpropan-1-imine) (11c). Hydrogen peroxide (0.78 mL of a 11.46 M solution in H_2O, 8.89 mmol) was added to a solution of **5c** (0.53 g, 0.89 mmol) in toluene (15 mL) at 0 °C, after which the reaction mixture was vigorously stirred for 30 min at room temperature. The toluene layer was isolated, and the water layer was extracted with 5 mL of toluene. The combined toluene layers were evaporated *in vacuo* to give a yellow solid. Crystallization from a minimal amount of diethyl ether at −20 °C gave two batches of yellow solid with a total yield of 0.52 g (0.85 mmol, 95%). Mp: 164.5 °C (dec). ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 8.09 (t, ^3J(H,H) = 8.5 Hz, 2H; *o*-PhH), 7.40 (t, ^3J(H,H) = 7.3 Hz, 1H; *p*-PhH), 7.34 (dt, ^4J(H,P) = 2.8 Hz, ^3J(H,H) = 7.3 Hz, 2H; *m*-PhH), 7.04−7.00 (m, 2H; *p*-ArH), 6.97−6.92 (m, 4H; *m*-ArH), 2.91 (sept, ^3J(H,H) = 6.6 Hz, 2H; $CH(CH_3)_2$), 2.43−2.31 (m, 2H; $CH(CH_3)_2$), 1.29 (s, 18H; $C(CH_3)_3$), 1.19 (d, ^3J(H,H) = 6.9 Hz, 6H; $CH(CH_3)_2$), 1.07−1.01 (m, 12H; $CH(CH_3)_2$), 0.62 (br s, 6H; $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 172.2 (N═C), 145.8 (d, ^3J(C,P) = 26.3 Hz; *ipso*-ArC), 134.1 (d, ^2J(C,P) = 7.3 Hz; *o*-PhC), 133.3 (s; *o*-ArC), 133.2 (s; *o*-ArC), 132.4 (d, ^1J(C,P) = 95.4 Hz; *ipso*-PhC), 131.1 (d, ^4J(C,P) = 1.8 Hz; *p*-PhC), 127.0 (d, ^3J(C,P) = 10.9 Hz; *m*-PhC), 123.2 (s; *m*-ArC), 122.9 (s; *m*-ArC), 122.6 (s; *p*-ArC), 46.4 (d, ^2J(C,P) = 29.1 Hz; $C(CH_3)_3$), 28.7 (d, ^3J(C,P) = 2.7 Hz; $C(CH_3)_3$), 28.5 (s; $CH(CH_3)_2$), 28.0 (s; $CH(CH_3)_2$), 24.9 (s; $CH(CH_3)_2$), 24.5 (s; $CH(CH_3)_2$), 22.6 (s; $CH(CH_3)_2$), 22.0 (s; $CH(CH_3)_2$). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 22.8 (s). IR: 2961 (m), 2924 (w), 2868 (w), 1636 (m), 1605 (w), 1587 (w), 1483 (m), 1460 (m), 1431 (m), 1394 (w), 1383 (w), 1360 (m), 1323 (w), 1258 (w), 1242 (w), 1205 (m), 1175 (s), 1161 (m), 1105 (m), 1097 (m), 1059 (w), 1041 (m), 966 (w), 956 (w), 937 (w), 800 (m), 760 (s), 744 (m), 710 (m), 698 (s), 675 (m), 644 (w), 590 (m), 571 (s), 554 (w), 507 (s), 498 (s). HR ESI-MS: calcd for $C_{17}H_{26}N$ (Dipp-N≡C-*t*Bu) 244.2060, found 244.2071. *m*/*z* (%): 244.2 (19) [Dipp-N≡C-*t*Bu]$^+$, 262.2 (100) [Dipp-N≡C-*t*Bu + H_2O]$^+$, 453.1 (2) [M − Dipp + 2H]$^+$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00063.

NMR spectra and geometries of computed structures (PDF)

Optimized Cartesian coordinates (XYZ)

X-ray crystallographic data for **5d** (CCDC-1433432) and **6** (CCDC-1433433) (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031−3066. (b) Tsai, Y.-C. *Coord. Chem. Rev.* **2012**, *256*, 722−758. (c) Landolsi, K.; Rzaigui, M.; Bouachir, F. *Tetrahedron Lett.* **2002**, *43*, 9463−9466. (d) Cope-Eatough, E. K.; Mair, F. S.; Pritchard, R. G.; Warren, J. E.; Woods, R. J. *Polyhedron* **2003**, *22*, 1447−1454. (e) Domin, D.; Benito-Garagorri, D.; Mereiter, K.; Hametner, C.; Fröhlich, J.; Kirchner, K. *J. Organomet. Chem.* **2007**, *692*, 1048−1057.

(2) Landolsi, K.; Elmkacher, N. B. M.; Guerfel, T.; Bouachir, F. *C. R. Chim.* **2008**, *11*, 752−758.

(3) (a) Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514−1516. (b) Liu, F.-S.; Gao, H.-Y.; Song, K.-M.; Zhang, L.; Zhu, F.-M.; Wu, Q. *Polyhedron* **2009**, *28*, 1386−1392. (c) Azoulay, J. D.; Gao, H.; Koretz, Z. A.; Kehr, G.; Erker, G.; Shimizu, F.; Galland, G. B.; Bazan, G. C. *Macromolecules* **2012**, *45*, 4487−4493.

(4) Domin, D.; Benito-Garagorri, D.; Mereiter, K.; Fröhlich, J.; Kirchner, K. *Organometallics* **2005**, *24*, 3957−3965.

(5) Kopylovich, M. N.; Pombeiro, A. J. L. *Coord. Chem. Rev.* **2011**, *255*, 339−355.

(6) (a) Masuda, J. D.; Stephan, D. W. *Can. J. Chem.* **2005**, *83*, 477−484. (b) Masuda, J. D.; Stephan, D. W. *Dalton Trans.* **2006**, 2089−2097. (c) Valdebenito, C.; Garland, M. T.; Quijada, R.; Rojas, R. *J. Organomet. Chem.* **2009**, *694*, 717−725. (d) For imino-pyrazoles as ligands in Ni(II)-catalyzed polymerization reactions see: Peoples, B. C.; De la Vega, G.; Valdebenito, C.; Quijada, R.; Ibañez, A.; Valderrama, M.; Rojas, R. *J. Organomet. Chem.* **2012**, *700*, 147−153.

DOI: 10.1021/acs.organomet.6b00063
Organometallics XXXX, XXX, XXX−XXX

(7) (a) Dias, H. V. R.; Singh, S. *Inorg. Chem.* **2004**, *43*, 7396−7402. (b) Dias, H. V. R.; Singh, S.; Cundari, T. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 4907−4910.
(8) (a) Heinicke, J.; Tzschach, A. *Z. Chem.* **1978**, *18*, 452−453. (b) Romanov, G. V.; Ryzhikova, T. Y.; Pudovik, A. N. *Zh. Obshchei Khim.* **1990**, *60*, 1718−1722.
(9) (a) Casares, J. A.; Espinet, P.; Hernando, R.; Iturbe, G.; Villafañe, F.; Ellis, D. D.; Orpen, A. G. *Inorg. Chem.* **1997**, *36*, 44−49. (b) Saucedo Anaya, S. A.; Hagenbach, A.; Abram, U. *Polyhedron* **2008**, *27*, 3587−3592. (c) Espinet, P.; Goómez-Elipe, P.; Villafañe, F. *J. Organomet. Chem.* **1993**, *450*, 145−150.
(10) (a) Inoguchi, Y.; Milewski-Mahrla, B.; Schmidbaur, H. *Chem. Ber.* **1982**, *115*, 3085−3095. (b) Xie, Y.; Lee, C.-L.; Yang, Y.; Rettig, S. J.; James, B. R. *Can. J. Chem.* **1992**, *70*, 751−762. (c) Lily Yun, X.; James, B. R. *Inorg. Chim. Acta* **1994**, *217*, 209−212. (d) Schutte, R. P.; Rettig, S. J.; Joshi, A. M.; James, B. R. *Inorg. Chem.* **1997**, *36*, 5809−5817. (e) Driess, M.; Franke, F.; Merz, K. *Eur. J. Inorg. Chem.* **2001**, *2001*, 2661−2668. (f) Casares, J. A.; Espinet, P.; Martín-Álvarez, J. M.; Santos, V. *Inorg. Chem.* **2006**, *45*, 6628−6636. (g) Adeyemi, O. G.; Liu, L.-K. *Inorg. Chim. Acta* **2009**, *362*, 477−482. (h) Zhang, T.; Ji, C.; Wang, K.; Fortin, D.; Harvey, P. D. *Inorg. Chem.* **2010**, *49*, 11069−11076. (i) Calhorda, M. J.; Ceamanos, C.; Crespo, O.; Gimeno, M. C. n.; Laguna, A.; Larraz, C.; Vaz, P. D.; Villacampa, M. D. *Inorg. Chem.* **2010**, *49*, 8255−8269. (j) Bakhoda, A.; Safari, N.; Amani, V.; Khavasi, H. R.; Gheidi, M. *Polyhedron* **2011**, *30*, 2950−2956. (k) Adeyemi, O. G.; Liu, L.-K. *Inorg. Chim. Acta* **2007**, *360*, 2464−2470.
(11) (a) Inoguchi, Y.; Milewski-Mahrla, B.; Neugebauer, D.; Jones, P. G.; Schmidbaur, H. *Chem. Ber.* **1983**, *116*, 1487−1493. (b) Newkome, G. R.; Evans, D. W.; Fronczek, F. R. *Inorg. Chem.* **1987**, *26*, 3500−3506. (c) Xie, Y.; James, B. R. *J. Organomet. Chem.* **1991**, *417*, 277−288.
(12) (a) van Dijk, T.; Burck, S.; Rong, M. K.; Rosenthal, A. J.; Nieger, M.; Slootweg, J. C.; Lammertsma, K. *Angew. Chem., Int. Ed.* **2014**, *53*, 9068−9071. (b) van Dijk, T.; Bakker, M. S.; Holtrop, F.; Nieger, M.; Slootweg, J. C.; Lammertsma, K. *Org. Lett.* **2015**, *17*, 1461−1464. (c) van Dijk, T.; Burck, S.; Rosenthal, A. J.; Nieger, M.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K. *Chem. - Eur. J.* **2015**, *21*, 9328−9331.
(13) CCDC 1433432 (**5d**) and 1433433 (**6**) 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. For the experimental details of the X-ray crystal structure determinations, see the Supporting Information.
(14) Equimolar amounts of the following salts ($CuCl_2$, $Cu(OTf)_2$, $ZnCl_2$, $ZnBr_2$, $Zn(SCN)_2$, $Zn(OTf)_2$) were mixed with **5b** in $CDCl_3$ in an NMR tube and measured with ^{31}P NMR.
(15) Arif, A. M.; Jones, R. A.; Seeberger, M. H.; Whittlesey, B. R.; Wright, T. C. *Inorg. Chem.* **1986**, *25*, 3943−3949.
(16) (a) For related phosphaalkene-oxazolines see: Dugal-Tessier, J.; Dake, G. R.; Gates, D. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 8064−8067. (b) Dugal-Tessier, J.; Dake, G. R.; Gates, D. P. *Org. Lett.* **2010**, *12*, 4667−4669. (c) Dugal-Tessier, J.; Serin, S. C.; Castillo-Contreras, E. B.; Conrad, E. D.; Dake, G. R.; Gates, D. P. *Chem. - Eur. J.* **2012**, *18*, 6349−6359.
(17) (a) Ito, S.; Kusano, S.; Morita, N.; Mikami, K.; Yoshifuji, M. *J. Organomet. Chem.* **2010**, *695*, 291−296. (b) Bartok, A.; Septelean, R.; Petrar, P. M.; Nemes, G.; Silaghi-Dumitrescu, L.; Ranaivonjatovo, H.; Mallet-Ladeira, S.; Saffon, N.; Hemmert, C.; Gornitzka, H. *J. Organomet. Chem.* **2013**, *724*, 200−205. (c) Siu, P. W.; Serin, S. C.; Krummenacher, I.; Hey, T. W.; Gates, D. P. *Angew. Chem., Int. Ed.* **2013**, *52*, 6967−6970.
(18) (a) Griesser, M.; Neshchadin, D.; Dietliker, K.; Moszner, N.; Liska, R.; Gescheidt, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 9359−9361. (b) Kolczak, U.; Rist, G.; Dietliker, K.; Wirz, J. *J. Am. Chem. Soc.* **1996**, *118*, 6477−6489. (c) Sluggett, G. W.; Turro, C.; George, M. W.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 5148−5153. (d) Jockusch, S.; Koptyug, I. V.; McGarry, P. F.; Sluggett, G. W.; Turro, N. J.; Watkins, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11495−11501. (e) Jockusch, S.; Turro, N. J. *J. Am. Chem. Soc.* **1998**, *120*, 11773−11777. (f) Huber, A.; Kuschel, A.; Ott, T.; Santiso-Quinones, G.; Stein, D.; Bräuer, J.; Kissner, R.; Krumeich, F.; Schönberg, H.; Levalois-Grützmacher, J.; Grützmacher, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 4648−4652.
(19) (a) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615−6620. (b) Chai, J.-D.; Head-Gordon, M. *J. Chem. Phys.* **2008**, *128*, 084106.
(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Ö. Farkas, Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.
(21) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724−728. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chem. Acc.* **1973**, *28*, 213−222. (d) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209−214. (e) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163−168. (f) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; DeFrees, D. J.; Pople, J. A.; Gordon, M. S. *J. Chem. Phys.* **1982**, *77*, 3654−3665. (g) Binning, R. C., Jr.; Curtiss, L. A. *J. Comput. Chem.* **1990**, *11*, 1206−1216. (h) Blaudeau, J.-P.; McGrath, M. P.; Curtiss, L. A.; Radom, L. *J. Chem. Phys.* **1997**, *107*, 5016−5021. (i) Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L. *J. Chem. Phys.* **1998**, *109*, 1223−1229. (j) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. *J. Comput. Chem.* **2001**, *22*, 976−984. (k) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294−301.
(22) Schafer, L. L.; Lauzon, J. M. P.; Ayinla, R. O.; P. Eisenberger WO Patent 2012/040853 A1, April 5, 2012.
(23) Upadhyaya, V.; Mahalakshmi, L.; Guru Row, T. N. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2002**, *58*, o997−o998.
(24) Loh, C.; Seupel, S.; Görls, H.; Krieck, S.; Westerhausen, M. *Organometallics* **2014**, *33*, 1480−1491.
(25) Cunico, R. F.; Pandey, R. K. *J. Org. Chem.* **2005**, *70*, 5344−5346.

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