Aromatic 1*H*-[1,2]Diphosphole with a Planar Tricoordinated Phosphorus, Plus η^2-Coordination Mode between Ruthenium(0) and a Phosphaalkene†

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1-(2,4,6-Tri-*tert*-butylphenyl)-1*H*-[1,2]diphosphole (**12**) was isolated from the unintentional and unexpected dehydrohalogenation of 1,3-bis(chloro(2,4,6-tri-*tert*-butylphenyl)phosphino)propane (**5**) with DBN. 1*H*-[1,2]Diphosphole **12** has substantial bond delocalization within the diphosphole system. Remarkably, the shortest P−C bond in the ring (1.725(4) Å) is observed for a nominal P−C single bond with the tricoordinated phosphorus atom. The P−P distance (2.0750(18) Å) in **12** is closer to the value for a P═P bond than for a P−P bond. The sum of the bond angles at the tricoordinated phosphorus atom in **12** is 351.3°, making **12** the most planar 1*H*-[1,2]diphosphole known to date. The ^{31}P NMR spectrum of **12** contains very similar chemical shifts for the tri- and dicoordinated phosphorus atoms (90.83 and 133.80 ppm), with a large P−P coupling constant ($^2J_{PP}$ = 528.2 Hz). This is further evidence of significant delocalization of the lone pair electrons of the tricoordinated phosphorus into the ring system and is consistent with the aromaticity of the 1*H*-[1,2]diphosphole ring in **12**. The reaction between ruthenium carbonyl and 8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine (**8**), which is the second product from the unexpected dehydrohalogenation, resulted in the formation of complex **27**, with a novel η^2-coordination mode between ruthenium and the phosphaalkene. The P−C bond in the three-membered ring of **27** is substantially lengthened by η^2-coordination, from 1.650(3) Å in the parent ligand to 1.775(3) Å in complex **27**.

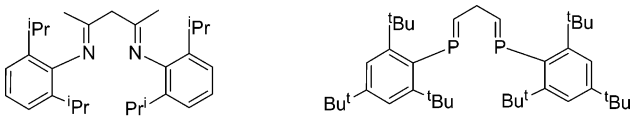
Introduction

N,N′-Chelating β-diketiminate ligands (e.g., **1**) have been shown to stabilize many transition elements and main group elements in unusual oxidation and coordination states.[1] Low-coordinated sp^2-hybridized phosphorus analogues of β-diketiminate ligands have yet to be synthesized. Compound **2** was chosen as the target ligand because replacing nitrogen with phosphorus was expected to increase the electron density on the metal, potentially leading to a wider range of catalytic applications for the corresponding metal complexes.[2] The 2,4,6-tri-*tert*-butylphenyl group was selected over the commonly used 2,6-di-isopropylphenyl group because the former has been shown to stabilize the P═C bonds more effectively.[3]

Results and Discussion

The synthetic methodology used to prepare 1,4-diphospha-1,3-butadienes initially developed by R. Appel was used to synthesize 1,5-diphospha-1,4-pentadiene (**2**).[4] 2,4,6-Tri-*tert*-butylphenyllithium (**3**) was reacted with commercially available 1,3-bis(dichlorophosphino)propane (**4**) to form 1,3-bis(chloro-(2,4,6-tri-*tert*-butylphenyl)phosphino)propane (**5**) (Scheme 2). The ^{31}P NMR spectrum of **5** consists of signals at 84.35 and 82.30 ppm, corresponding to two diastereomers. In an attempt to synthesize compound **2**, two sequential dehydrohalogenations of **5** by 1,5-diazabicyclo[4.3.0]non-5-ene (**6**) (DBN) were conducted. Although DBN usually behaves as a non-nucleophilic strong base,[5] it can also act as a nucleophile.[6] The first dehydrohalogenation of **5** produced intermediate **7**. Further reaction of **7** with DBN, however, involved two competing pathways. In one, 8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]-phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine (**8**) was formed, when DBN reacted as a C-nucleophile with intermediate **7**. In the second

Scheme 1



1 **2**

† This is DuPont contribution # 8782.

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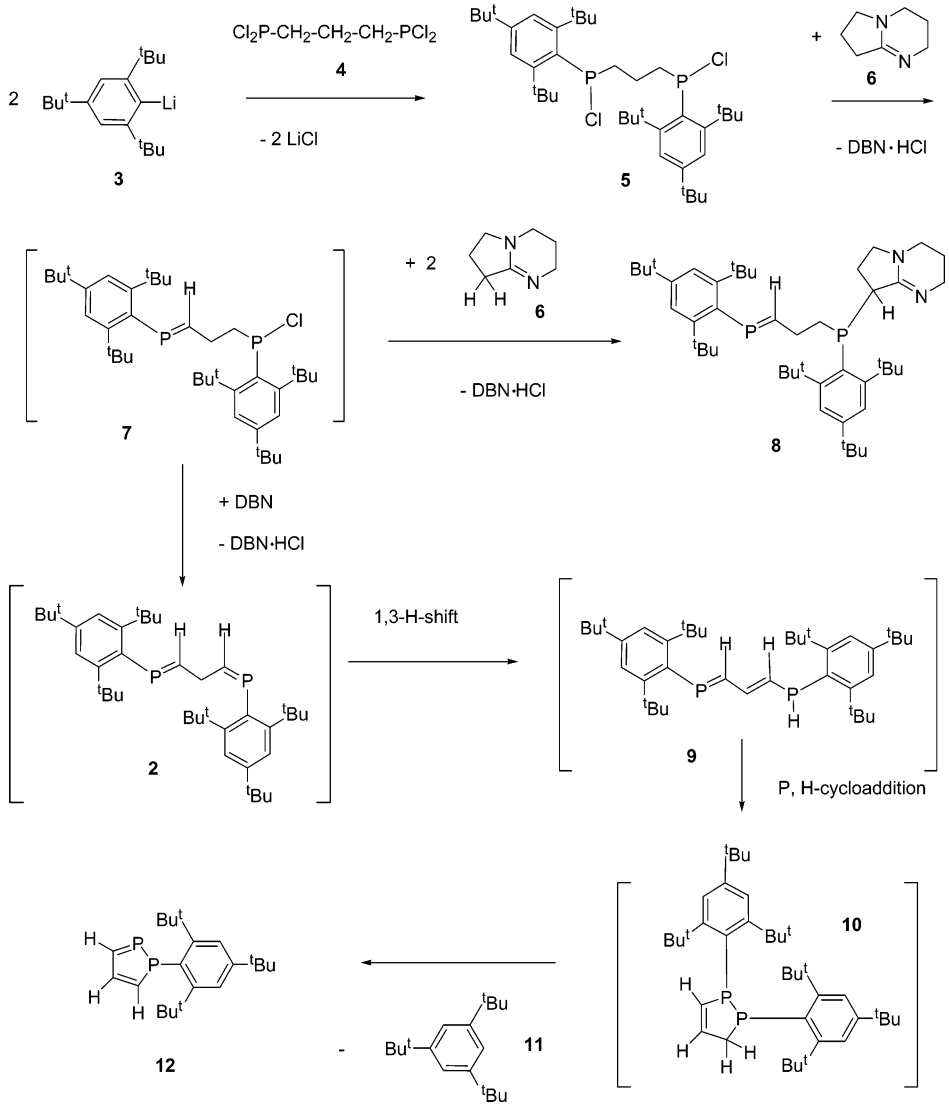
Scheme 2



pathway, the expected doubly dehydrohalogenated compound **2** apparently was formed, but was not stable and presumably underwent a 1,3-hydrogen shift from carbon to phosphorus to form P−H intermediate **9**. Compound **9** likely underwent P,H cycloaddition with formation of a highly sterically strained intermediate **10**. DBN is known to catalyze 1,3-hydrogen shifts[7] and P,H-addition to double bonds.[8] Relief of steric bulk by elimination of 1,3,5-tri-*tert*-butylbenzene[9] (**11**) from **10** would lead to the other stable product, 1-(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2]diphosphole (**12**). The chemistry of sp^2-hybridized phosphapolyenes is known for its unusual cyclic products, either through phospha-Cope rearrangements or through cycloadditions.[10]

The ^{31}P NMR spectrum of **8** consists of two singlets: a downfield signal for the phosphaalkene at 248.78 ppm and an upfield signal for the phosphine moiety at −15.97 ppm. The phosphaalkene moiety in **8** has a typical ^{13}C NMR downfield signal at 181.90 ppm, with two carbon−phosphorus coupling constants ($^1J_{PC}$ = 36.4 Hz and $^3J_{PC}$ = 19.0 Hz). The ^{1}H NMR resonance (7.45 ppm) of hydrogen attached to the sp^2 carbon of **8** is a doublet of triplets, with a hydrogen−phosphorus coupling constant ($^2J_{PH}$ = 25.5 Hz) and a vicinal hydrogen−hydrogen coupling constant ($^3J_{HH}$ = 8.3 Hz). A full multinuclear interpretation of NMR data for **8** can be found in the Experimental Section.

According to X-ray analysis, compound **8** exists as the sterically less strained *E*-isomer (Figure 1). The P−C double bond length is 1.650(3) Å, which is slightly shorter than the average value of 1.67 Å for P−C double bonds.[3b] The single P−C bond length in the central P═C−C−C−P fragment is 1.849(2) Å.

NMR and structural data (Figure 2 and Table 1) for 1-(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2]diphosphole (**12**) were found to be quite unusual. The structural peculiarity of **12** can be directly connected to two heavily contested issues in organophosphorus chemistry: the planarity of a tricoordinated phosphorus atom[11] and P^{III} to P^{V} valence isomerism.[12] The majority of known trivalent tricoordinated phosphorus compounds are pyramidal. In these compounds, the phosphorus lone pair of electrons has a large "s" character and is unable to participate in conjugation

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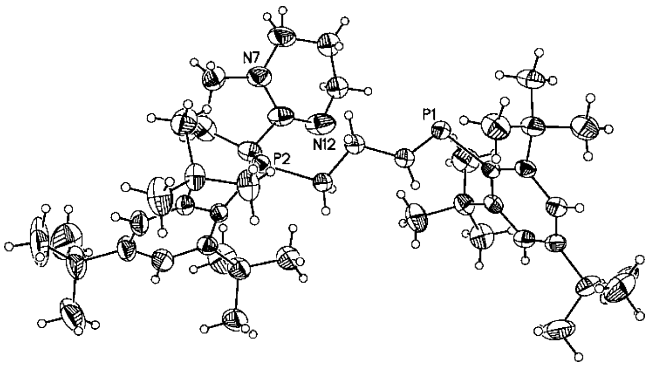


Figure 1. ORTEP drawing of 8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]-phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine, **8**. A crystal was grown from toluene. Thermal ellipsoids are drawn at the 50% probability level.

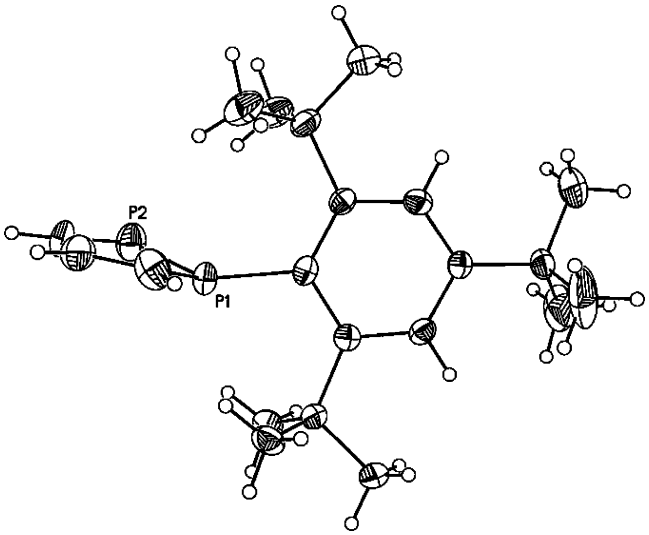
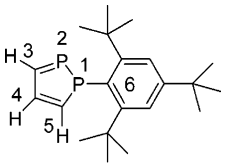


Figure 2. ORTEP drawing of 1-(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2]diphosphole, **12**. A crystal was grown from pentane. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Lengths and Angles for 12



12

type of bond	bond length (Å)	type of angle	angle (deg)
P1−P2	2.0750 (18)	C(5)−P(1)−P(2)	100.85(17)
P2−C3	1.732 (5)	C(5)−P(1)−C(6)	120.31(19)
C3−C4	1.412 (7)	C(6)−P(1)−P(2)	130.10(12)
C4−C5	1.349 (6)	C(4)−C(5)−P(1)	110.8(4)
C5−P1	1.725 (4)	C(3)−P(2)−P(1)	88.84(18)
P1−C6	1.824(4)	C(4)−C(3)−P(2)	119.7(3)

with π-systems. The introduction of sterically hindered groups at the phosphorus has been shown to increase the degree of planarity of the phosphorus atom incorporated in a ring system. The additional presence of two-coordinated phosphorus atoms in five-membered rings was found to increase the degree of planarity of the tricoordinated phosphorus, e.g., in 1,2,4-triphospholes. Planar phospholes are expected to be highly aromatic, and therefore the chemical reactivity, spectral, and geometrical properties are expected to be different from nonplanar phospholes.[13] In spite of their aromaticity, planar phospholes are not expected to be chemically inert. The destruction of the aromatic system of such phospholes in any chemical reaction can be compensated by the energetically favorable pyramidalization of the tricoordinated phosphorus or an oxidation reaction of the phosphorus lone pair of electrons.[13b]

Schmidpeter's method of measuring the degree of phosphorus planarity was used to evaluate the planarity of **12**.[12b] This method calculates the sum of bond angles at the phosphorus atom, and higher numbers correspond to greater phosphorus planarity (Scheme 3). The gradual flattening of the phosphorus pyramid from **13** (314.4°) to **15** (331.7°) can be attributed to increasing steric hindrance of the *ortho*-substituents in this series of aryl phospholes.[11] Introduction of a sp^2 phosphorus into a five-membered-ring compound with electron-withdrawing triphenylphosphonium substituents (**16**) resulted in a Schmidpeter number of 339.0°.[12b] Diphosphole **12** has a Schmidpeter number of 351.3°, indicating that it is the most planar diphosphole to date. Triphosphole **17** still has the most planar tricoordinate phosphorus atom known, presumably because there are two sp^2 phosphorus atoms in the five-membered ring.[11d]

Remarkably, the shortest P−C bond in the diphosphole ring of **12** is that of the P1−C5 bond (1.725(4) Å), which is nominally a P−C single bond. A similar effect was observed for phosphole **17**.[11d] The P−P distance (2.0750(18) Å) in **12** is closer to the value for a P═P double bond (2.034(2) Å in Yoshifuji's original diphosphene) than for a P−P single bond (2.22 Å).[3c] The nominal P═C double bond length in **12** (1.732(5) Å) is longer than the average value of 1.67 Å for P−C double bonds[3b] and is also longer than the C═P double bond in **8** (1.650(3) Å), reflecting the delocalization of this bond within the diphosphole system.

The ^{31}P NMR spectrum of **12** contains very similar chemical shifts for the tri- and dicoordinated phosphorus atoms (90.83 and 133.80 ppm), with a large phosphorus−phosphorus coupling constant ($^2J_{PP}$ = 528.2 Hz). Such large P−P couplings are commonly found for cyclic and acyclic diphosphenes.[3c,11d] The P−P coupling for a direct P−P single bond is observed around 220 Hz.[14] This is a further indication of significant delocalization of the lone pair electrons of the tricoordinated phosphorus into the ring system. The same phenomenon was noted for the delocalized 1,2,4-triphosphole with the planar tricoordinate phosphorus.[11d]

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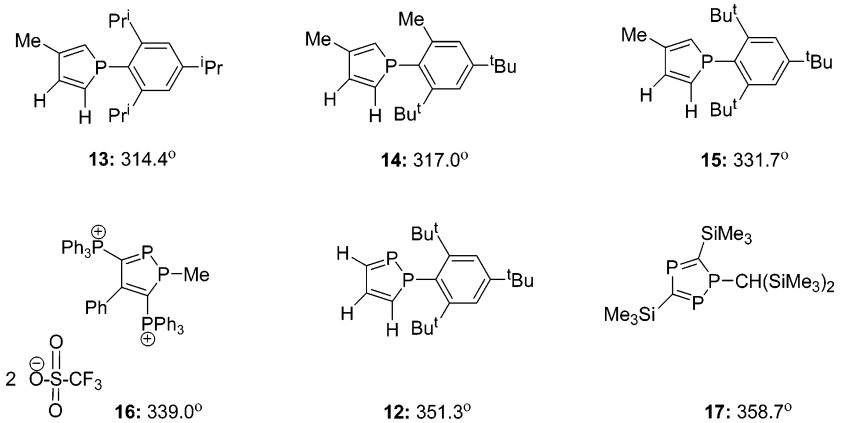
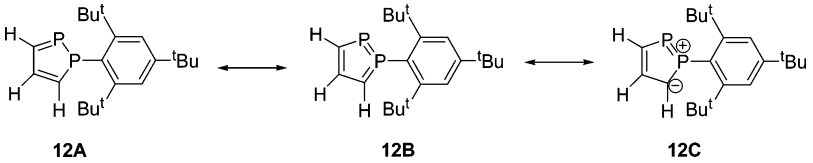
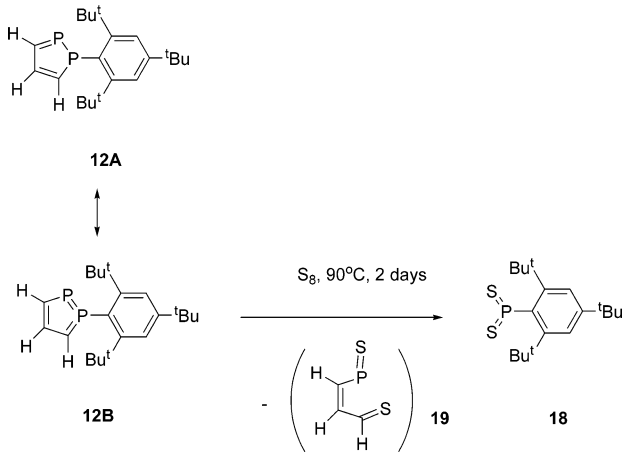
Scheme 3. Planarity of the Phosphorus Atoms in Selected Phospholes (12−17) Calculated by Schmidpeter's Method



Scheme 4. Possible Resonance Structures Describing the Bonding in Planar Diphosphole 12



Scheme 5



The observed bond lengths of the diphosphole ring and the NMR data of **12** are consistent with the aromaticity and the geometry of the ring and are also consistent with valence isomerism involving the five-valent canonical form **12B** (Scheme 4).

Valence isomerism, which can be defined as the synchronous shift of σ- and/or π-electrons without migration of atoms or groups, has a prominent role in heterocyclic chemistry.[12] It can be invoked in our diphosphole structural characterization as an example of the P^{III} to P^{V} valence isomerism.[13a] The contribution of canonical structure **12B** can be evidenced by the oxidation reaction of **12** with elemental sulfur. No reaction was observed at room temperature, pointing to the relative stability of **12** toward oxidation. However, prolonged heating of **12** with elemental sulfur resulted in the rupture of P−P and P−C bonds and the destruction of the aromatic system. Dithiooxo(2,4,6-tri-*tert*-butylphenyl)phosphorane (**18**) (Scheme 5) was observed as the stable product. This oxidation resembles ozonolysis of nitrogen-containing aromatic systems, which takes place with rupture of double bonds.[15]

The presence of dithiooxo(2,4,6-tri-*tert*-butylphenyl)phosphorane (**18**) in the reaction mixture was confirmed by ^{31}P NMR. When a known sample of dithiooxo(2,4,6-tri-*tert*-butylphenyl)phosphorane (**18**), prepared by a literature procedure from elemental sulfur and 2,4,6-tri-*tert*-butylphenylphosphine,[16b] was added to the reaction mixture, the ^{31}P NMR signals coincided at 299.50 ppm.[16] Compound **18** was also identified by mass spectrometry (ASAP MS method),[17] which gave an MH^+ ion at 341.15, corresponding to $C_{18}H_{30}PS_2$. The plausible intermediate **19**, which might be formed upon scission of the diphosphole ring, is probably thermodynamically unstable, and attempts to identify it were unsuccessful. No monosulfides of **12**, or [2+4] cycloaddition dimers (Diels−Alder dimer) of monosulfides, were detected, as expected from the common chemistry of phospholes without substantial aromatization.[18]

Although it is not a direct phosphorus analogue of β-diketiminate ligands, compound **8** contains several coordination centers: two phosphorus lone pairs, two nitrogen lone pairs, and P═C and C═N double bonds. This donor ability, combined with the chelating effect of **8**, can lead to new coordination modes of the transition elements and, in the long term, to new catalytic properties of such complexes. For this reason we explored the reactions of **8** with both silver triflate **20** and a complex of nickel(II) bromide with 2-methoxyethyl ether (**21**) (Scheme 6).

In both reactions, compound **8** behaved as a strong base. Trifluoromethanesulfonate 8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidin-1-ium (**23**) and 1-{3-[2,6-bis(2,4,6-tri-*tert*-butylphenyl)[1,2,6]azadiphosphinan-1-yl]propyl}pyrrolidin-2-one (**24**) were isolated, along with metallic silver, from the reaction of **8** with silver triflate **20**. An analogous bromide salt, **25**, was isolated from the reaction of **8** with a complex of nickel(II) bromide with 2-methoxyethyl ether (**21**). Reduction of Ag(I) to metallic silver by phoshines

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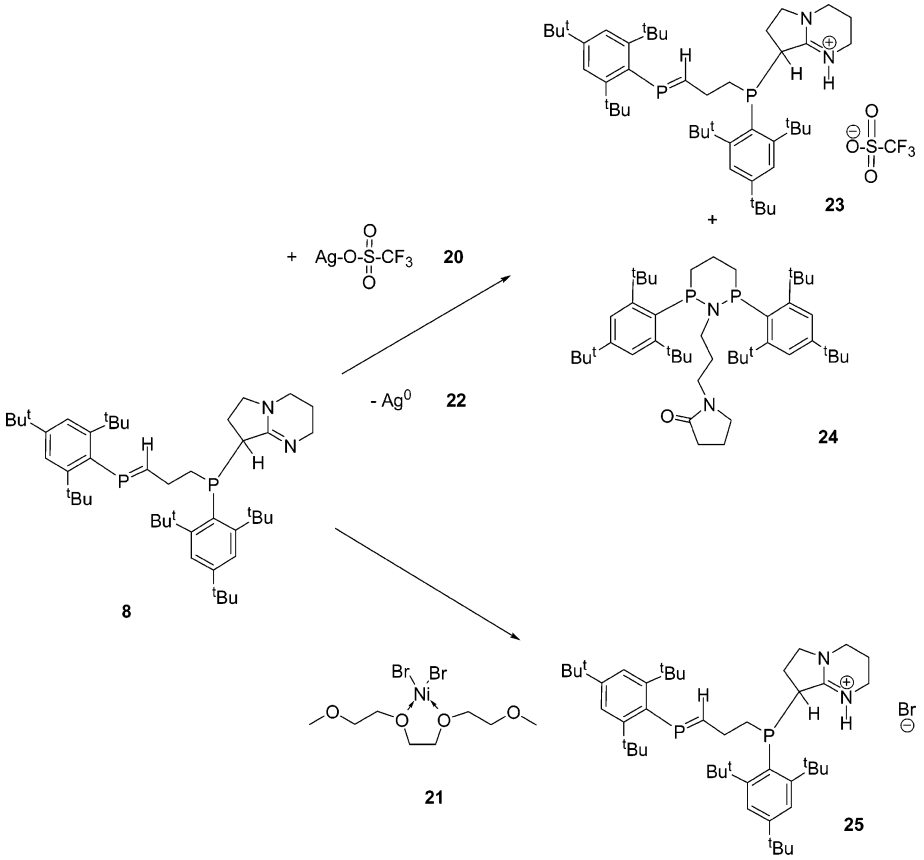
Scheme 6



is known and widely used for the chemical vapor deposition (CVD) of silver films.[19] Trialkyl triflates are known, although very rarely, to react with DBN, resulting in ring-opening of the enamine moiety of DBN to form lactam derivatives, with further cleavage of C−C bonds.[20] It is likely that the same ring-opening mechanism with P−C bond cleavage took place upon reaction of silver triflate with **8**. Compound **24** can be formed by the addition of the exocyclic amino moiety of the lactam from DBN to the two C═P bonds of compound **2** generated in this reaction. An alternative pathway to **24** can be envisioned starting from the triflate salt **23** through ring-opening of the DBN moiety in **23** and P−C bond cleavage. At the present time we do not have sufficient evidence to speculate on a stepwise mechanism for the formation of compound **24**. Reduction of nickel(II) compounds to metallic nickel by phosphorus compounds is known, and it may be taking place here.[21] We did not isolate metallic nickel from this reaction.

The structures of **23**, **24**, and **25** were investigated by X-ray analysis (Figure 3, 4, and 5). Preservation of the P═C double bond was observed in both salts **23** and **25**. The proton is connected with the nitrogen atom of the DBN moiety in **23** and **25**. The sp^2 and sp^3 phosphorus atoms in **8** are less basic than the sp^2 nitrogen atom in the DBN moiety of **8**. The nominal P═C double bond lengths in **23** and **25** are 1.624(8) and 1.658(3) Å, respectively, which are close to the value for the parent ligand (1.650(3) Å, Table 2). The geometry around the C═P bond in salts **23** and **25** is different from that of the starting ligand. Solid-state samples of **23** and **25** are *Z*-isomers, whereas the parent ligand **8** consists of an *E*-isomer. According to the ^{31}P NMR spectrum of **23**, it exists in acetonitrile solution as a 2:1 mixture of two isomers with two sets of singlets at 247.83 and −13.63 ppm (major isomer) and at 246.57 and −15.41 ppm (minor isomer). Two isomers were observed in solutions of **25**,

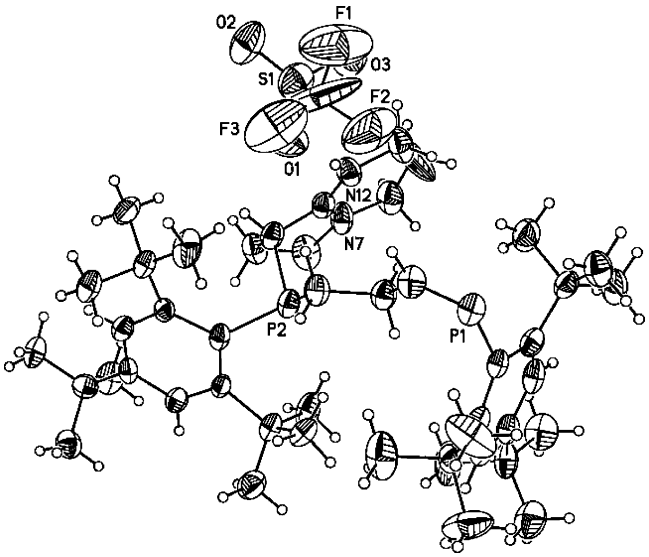


Figure 3. ORTEP drawing of trifluoromethanesulfonate 8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)-propyl]-phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidin-1-ium, **23**. A crystal was grown from pentane. Thermal ellipsoids are drawn at the 50% probability level.

(19) (a) Edwards, D. A.; Harker, R. M.; Mahon, M. F.; Molloy, K. C. *Inorg. Chim. Acta* **2002**, *328*, 134. (b) Edwards, D. A.; Harker, R. M.; Mahon, M. F.; Molloy, K. C. *J. Mater. Chem.* **1999**, *9*, 1771. (c) Szczesny, R.; Szymanska, I.; Piszczek, P.; Dobrzanska, L.; Szlyk, E. *Mater. Sci.* **2005**, *23*, 671.

(20) (a) Ma, L.; Dolphin, D. *Tetrahedron* **1996**, *52*, 849. (b) Lammers, H.; Cohen-Fernandes, P.; Habraken, C. L. *Tetrahedron* **1994**, *50*, 865.

(21) (a) Chernogorenko, V. B.; Muchnik, S. V.; Kogan, B. S.; Donets, I. G.; Lynchak, K. A.; Serdyuk, V. A.; Dolinina, I. V. *Zh. Neorg. Khim.* **1986**, *31*, 1502. (b) Matsuda, K.; Yamada, K.; Kato, C.; Fujita, K. *Proc. Sch. Sci. Tokai Univ.* **2001**, *36*, 61.

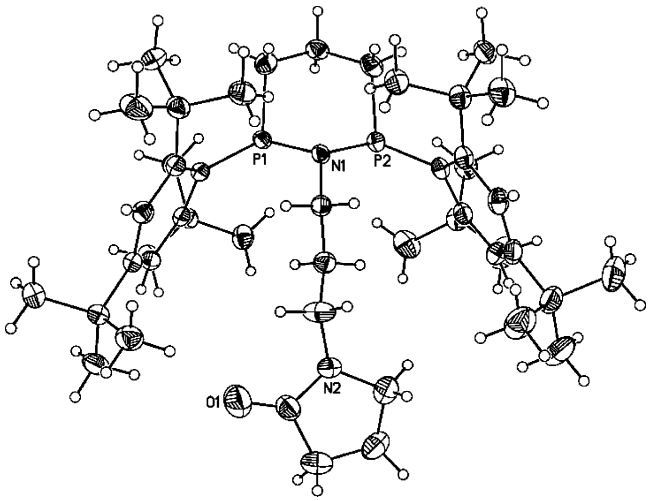


Figure 4. ORTEP drawing of 1-{3-[2,6-bis(2,4,6-tri-*tert*-butylphenyl)-[1,2,6]azadiphosphinan-1-yl]propyl}pyrrolidin-2-one, **24**. A crystal was grown from pentane. Thermal ellipsoids are drawn at the 50% probability level.

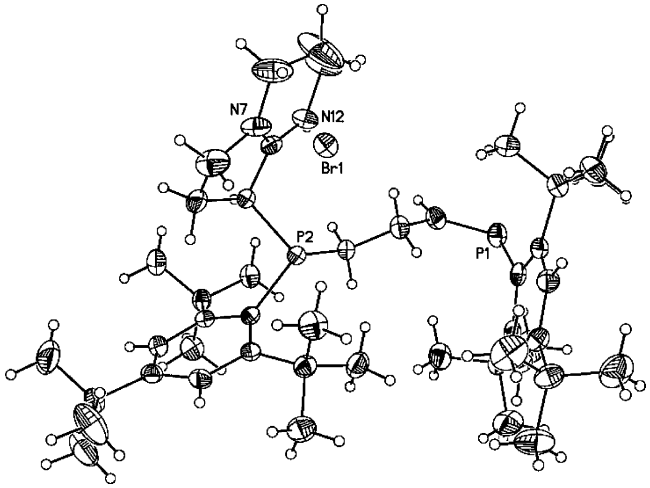


Figure 5. ORTEP drawing of 8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidin-1-ium bromide, **25**. A crystal was grown from dichloromethane. Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Lengths and Angles for 8, 23, 25, and 27

compound	C═P bond length (Å)	geometry of C═P bond	P═C─C angle (deg)
8	1.650(3)	*E*-isomer	125.0(2)
23	1.624(8)	*Z*-isomer	133.3(7)
25	1.658(3)	*Z*-isomer	132.2(2)
27	1.775(3)	η^2-coordination	124.3(2)

but in a ratio of 9:1. *E*,*Z*-Isomerization in phosphaalkenes has been detected before and is likely catalyzed here by the acidic proton of salts **23** and **25**.[3] *Z*-Isomers are probably more favorable upon packing in the crystal unit cells.

To avoid formation of salts like **23** and **25**, a zerovalent metal precursor was selected for complexation with **8**. Ruthenium carbonyl **26** reacted smoothly with **8**, leading to formation of complex **27** (Scheme 7). Ligation between ruthenium and the C═P moiety in **27** can be described as η^1-coordination (via the lone pair of phosphorus) or η^2-coordination (via the π-system of the phosphaalkene). ^{31}P NMR spectrometry is a useful tool to distinguish between these two possible modes of coordination.[22] The η^1-coordination mode is the most extensively reported for phosphaalkenes.[3,22] The ^{31}P NMR chemical shifts of such complexes do not change much from the resonances of the parent ligands, which are typically observed downfield. The η^2-coordination mode is relatively rare, and the ^{31}P NMR chemical signals are shifted significantly upfield. For example, resonances at 23.40 ppm for η^2-Ni and at − 80.00 ppm for η^2-Pt were reported.[23,24] No ^{13}C NMR spectrometry data have been reported for the η^2-fragment of phosphaalkene complexes.

The ^{31}P NMR spectrum of **27** (with a wide sweep from 1000 to −600 ppm) revealed only two doublets at 53.77 and 31.79 ppm with the same phosphorus−phosphorus coupling constant ($^2J_{PP}$ = 36.9 Hz). The ^{31}P NMR resonance of the sp^2 phosphorus atom in the parent ligand **8** appears at 248.78 ppm. Thus, an upfield shift of the resonance of the sp^2 phosphorus atom took place upon coordination with ruthenium, suggesting an η^2-coordination mode. A marked upfield shift in the ^{13}C NMR of the sp^2 carbon atom from 181.90 ppm in the parent ligand **8** to 63.19 ppm in the ruthenium complex **27** also suggests an η^2-coordination mode. It should be noted that the carbon−phosphorus coupling in the η^2-moiety of **27** has a relatively large value of 70.3 Hz, which is typical of other types of three-membered rings containing phosphorus.[3b] Two terminal CO groups in **27** show bands at 1958 and 1880 cm^{-1} in the IR spectrum. The CO groups appear as two downfield doublets in the ^{13}C NMR spectrum at 213.20 ppm ($^2J_{PC}$ = 10.0 Hz) and 203.07 ppm ($^2J_{PC}$ = 5.4 Hz).

The structure of **27** was determined by single-crystal X-ray diffraction. The ORTEP drawing of complex **27** is shown in Figure 6 and reveals the geometry at ruthenium approximating trigonal bipyramid. Two phosphorus atoms are located *trans* to each other at ruthenium and occupy two equatorial sites. Two carbonyl groups are in *cis* positions at ruthenium. One carbonyl occupies the equatorial position and one carbonyl occupies the axial position. Nitrogen occupies the second axial position. We believe that the geometry of this isomer is largely determined by the steric hindrance of the tridentate ligand. The η^2-coordination mode of the P═C moiety to ruthenium leads to a bent trigonal bipyramidal geometry. The distances between ruthenium and phosphorus and between ruthenium and carbon in the P/Ru/C three-membered ring are 2.4370(9) and 2.182(3) Å, respectively, which are within the normal range for such bonds.[25] In contrast, the P−C bond in the three-membered ring is substantially lengthened by η^2-coordination, from 1.650(3) Å in the parent ligand to 1.775(3) Å in **27**. In η^1-complexes, the P−C bond length is comparable to that of the free phosphaalkene ligands.[22]

Historically, the first ethylene complexes with ruthenium were prepared using ligands in which the olefin was part of a chelating ligand (e.g., 2-vinylphenyl(diphenyl)phosphine)[26] or in which the olefin had strongly electron-withdrawing groups (e.g., tetrafluoroethylene).[27] Ligand **8** is an example of a chelating ligand with a phosphaalkene group, and the chelating effect may

(22) (a) Nixon, J. F. *Chem. Rev.* **1988**, *88*, 1327. (b) Floch, P. L. *Coord. Chem. Rev.* **2006**, *250*, 627.

(23) Cowley, A. H.; Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 7015.

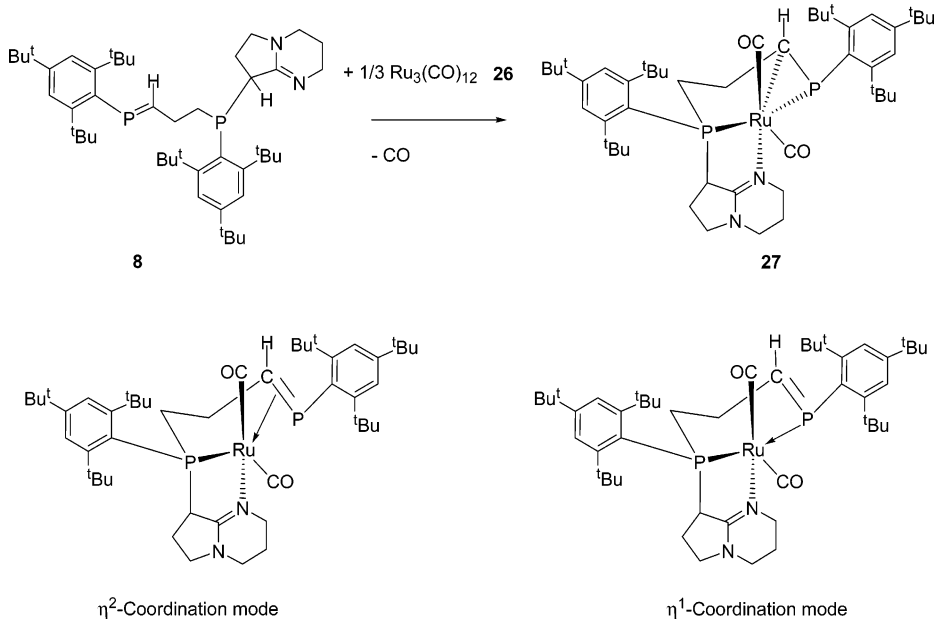
(24) Benvenutti, M. H.; Cenac, N.; Nixon, J. F. *Chem. Commun.* **1997**, 1327.

(25) (a) Dewhurst, R. D.; Hill, A. F.; Rae, A. D.; Willis, A. C. *Organometallics* **2005**, *24*, 4703. (b) Barlett, M. J.; Hill, A. F.; Smith, M. K. *Organometallics* **2005**, *24*, 5795. (c) Ogasawara, M.; Maseras, F.; Gallego-Planas, N.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 7468.

(26) Bennett, M. A.; Robertson, G. B.; Tomkins, I. B.; Whimp, P. O. *Chem. Commun.* **1971**, 341.

(27) Burt, R.; Cooke, M.; Green, M. *J. Chem. Soc. (A)* **1970**, 2975.

Scheme 7



help to stabilize the novel η^2-coordination mode between ruthenium and phosphaalkene. The η^1- and η^3-coordination modes between phosphaalkene and divalent ruthenium have been described recently.[28] The determination of the catalytic properties of **27** is under way and will be reported shortly.

Experimental Section

All air-sensitive compounds were prepared and handled under a N_2/Ar atmosphere using standard Schlenk and inert-atmosphere glovebox techniques. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through columns under an argon or nitrogen atmosphere. 1,5-Diazabicyclo-[4.3.0]non-5-ene (DBN), 2-bromo-1,3,5-tri-*tert*-butylbenzene, nickel(II) bromide as a complex with 2-methoxyethyl ether, elemental sulfur, silver trifluoromethanesulfonate, dichloromethane (anhydrous, >99.8%), and THF were purchased from Aldrich. 1,3-Bis-(dichlorophosphino)propane was purchased from Digital Specialty Chemicals, Inc. Ruthenium carbonyl was purchased from Strem, Inc. Melting points are uncorrected. All ^{1}H, ^{13}C, ^{13}C Dept135, Cosy 45, TOCSY, HMQC, and HMBC spectra of **27** were run in toluene-d_8 on a Bruker500 AMX using an inverse broadband probe at 50 °C. The parameters used in these experiments are given in the Supporting Information. All experiments run on this sample used pulse sequences found in the Bruker pulse sequence library, and their names are listed on the spectra. The mass spectra were collected on an Orbitrap mass spectrometer (ThermoFisher Scientific, Breman, Germany).

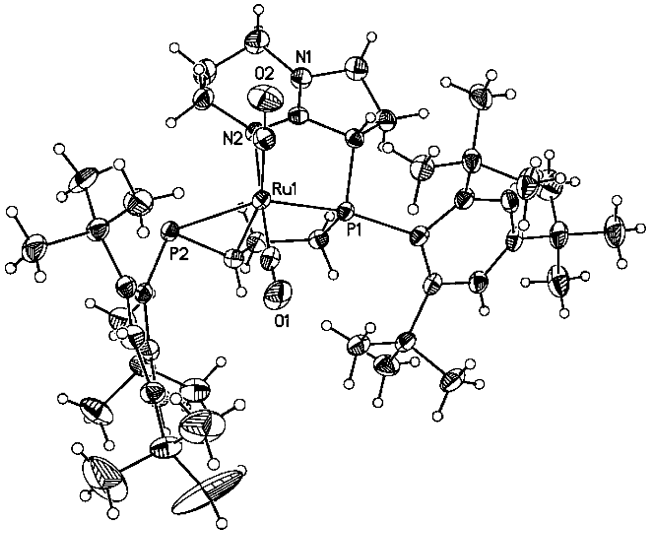


Figure 6. ORTEP drawing of (dicarbonyl)[8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]-phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine] ruthenium(0), **27**. A crystal was grown from toluene. Thermal ellipsoids are drawn at the 50% probability level.

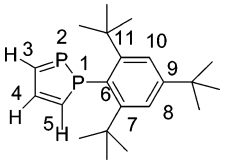
1,3,5-Tri-*tert*-butylbenzene (11), 1-(2,4,6-Tri-*tert*-butylphenyl)-1*H*-[1,2]diphosphole (12), and 8-{(2,4,6-Tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine (8). A solution of 7.5 g (0.0231 mol) of 2-bromo-1,3,5-tri-*tert*-butylbenzene was dissolved in 100 mL of THF under argon. The flask was then cooled to −78 °C, and 16 mL of a 1.6 M hexane solution of BuLi was added via syringe. The resulting mixture was stirred at −78 °C for 2 h. Then 2.5 g (0.010 mol) of 1,3-bis(dichlorophosphino)propane (**4**) was added to the reaction mixture via syringe, and the flask was allowed to slowly warm to room temperature overnight. Monitoring the progress of the reaction by ^{31}P NMR spectrometry revealed that the signal of the starting 1,3-bis(dichlorophosphino)-propane disappeared and a new pair of signals appeared at 84.35 and 82.30 ppm, corresponding to intermediate 1,3-bis(chloro(2,4,6-tri-*tert*-butylphenyl)phosphino)propane (**5**). The solvent was removed at 1 mmHg *in vacuo*, and the remaining reaction mixture was passed into the nitrogen glovebox. The mixture was dissolved in 200 mL of toluene and filtered, and then 6.6 g (0.053 mol) of DBN (**6**) was added to the filtrate. The color of the reaction mixture changed from yellow to red. The reaction mixture was heated at 90 °C for about 3 days until the signals of 1,3-bis(chloro(2,4,6-tri-*tert*-butylphenyl)phosphino)propane (**5**) disappeared. Then, the mixture was purified by chromatography on silica gel, starting with hexane as eluent and increasing the polarity of the eluent to 20% ethyl ether and 80% hexane. The following fractions were collected in order of elution.

1,3,5-Tri-*tert*-butylbenzene (11): white solid with mp 71.1 °C. The yield of **11** was 1.31 g (23%). ^{1}H NMR (500 MHz, C_6D_6,

(28) (a) Hitchcock, P. B.; Jones, C.; Nixon, J. F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 463. (b) Bedford, R. B.; Hill, A. F.; Jones, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 547.

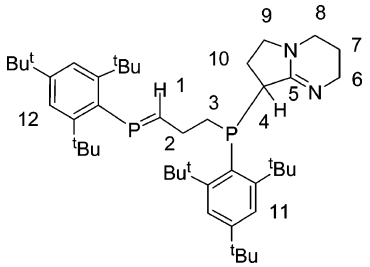
TMS): δ 1.40 (s, 27H, Me), 7.34 (s, 3H, arom H). ^{1}H NMR spectral data and melting point of **11** were close to known numbers.[29]

1-(2,4,6-Tri-*tert*-butylphenyl)-1*H*-[1,2]diphosphole (12). The yield of **12** was 2.46 g (31% on the starting 2-bromo-1,3,5-tri-*tert*-butylbenzene) as yellow crystals with mp 108.6 °C.

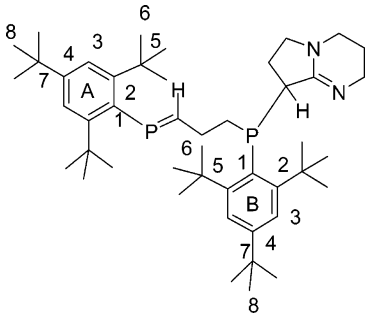


^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 8.15 (dddd, $^2J_{PH}$ = 45.8 Hz; $^3J_{PH}$ = 27.2 Hz; $^3J_{HH}$ = 6.8 Hz; $^4J_{HH}$ = 1.1 Hz, 1H, H-3); 7.60 (d, $^4J_{PH}$ = 4.3 Hz; 2H, H-8 and H-10); 7.46 (dddd, $^2J_{PH}$ = 38.6 Hz; $^3J_{PH}$ = 13.8 Hz; $^3J_{HH}$ = 6.8 Hz; $^4J_{HH}$ = 1.1 Hz, 1H, H-5); 7.58 (dddd, $^3J_{PH}$ =3.5 Hz; $^3J_{PH}$ = 27.2 Hz; $^3J_{HH}$ = 6.8 Hz; $^3J_{HH}$ = 6.8 Hz, 1H, H-4); 1.24 (s, 18H, Me); 1.20 (s, 9H, Me). ^{1}H and ^{13}C two-dimensional NMR experiment (500 MHz, CD_2Cl_2): δ C−H atoms of 1,2-diphosphole ring: C-3: 146.70 (dd, $^1J_{PC}$ = 62.8 Hz, $^2J_{PC}$ = 23.7 Hz), correlates with ^{1}H NMR signal at 8.15 ppm; C-4: 134.26 (d, $^1J_{PC}$ = 30.2 Hz, $^2J_{PC}$ = 1.4 Hz), correlates with ^{1}H NMR signal at 7.46 ppm; C-5: 131.10 (dd, $^1J_{PC}$ = 30.5 Hz, $^2J_{PC}$ = 14.4 Hz), correlates with ^{1}H NMR signal at 7.58 ppm; aromatic carbons of benzene ring: C-6 (*ipso*-carbon): 117.7 (dd, $^1J_{PC}$ = 25.0 Hz, $^2J_{PC}$ = 5.0 Hz); non-H carbons: C-7 and C-11 (*ortho*-carbons): 159.35 (dd, $^2J_{PC}$ = 8.7 Hz, $^3J_{PC}$ = 1.1 Hz); C-8 and C-10 (*meta*-carbons): 123.60 (d, $^3J_{PC}$ = 11.5 Hz), correlates with ^{1}H NMR doublet at 7.60 ppm; C-9 (*para*-carbon): 154.41 (d, $^2J_{PC}$ = 3.4 Hz); carbon atoms of *tert*-butyls: tertiary-C: 39.00 (d, $^3J_{PC}$ = 3.2 Hz); *para*-C: 37.50 (s); methyls: 32.00 and 33.70. ^{31}P NMR (500 MHz, CD_2Cl_2): δ 90.83 (d, $^2J_{PP}$ = 528.2 Hz, 1P), 133.80 (d, $^2J_{PP}$ = 528.2 Hz, 1P). The structure was determined by X-ray analysis.

8-{(2,4,6-Tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo-[1,2-*a*]pyrimidine (8). The yield of **8** was 3.47 g (42% on the starting 2-bromo-1,3,5-tri-*tert*-butylbenzene) as yellow crystals with mp 185.0 °C.



^{1}H NMR and ^{13}C NMR spectra for the central fragment of the molecule (from H−^{13}C HSQC one-bond correlation experiment): ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 7.45 (d, t, $^2J_{PH}$ = 25.5 Hz; $^3J_{HH}$ = 8.3 Hz 1H, H-1), 7.39 (d, $^4J_{HH}$ = 0.6 Hz, 2H, H-11), 7.31 (d, $^4J_{HH}$ = 0.5 Hz, 2H, H-12), 3.29 (br, 1H, H-4), 3.24 (br, 2H, H-8), 3.15 (br, 1H, H-9), 3.10 (br, 2H, H-6), 2.90 (br, 1H, H-9), 2.85 (br, 1H, H-3), 2.27 (br, 1H, H-3), 2.27 (br, 2H, H-2), 1.70 (br, 2H, H-7), 1.52 (s, 18H, Me), 1.53 (s, 18H, Me), 1.34 (s, 9H, Me), 1.30 (s, 9H, Me), 1.50 (br, 1H, H-10), 0.53 (br, 1H, H-10). ^{13}C NMR (500 MHz, CD_2Cl_2): 181.90 (dd, $^1J_{PC}$ = 36.4 Hz, $^3J_{PC}$ = 19.0 Hz, C-1), 36.11 (dd, $^2J_{PC}$ = 37.0 Hz, $^2J_{PC}$ = 28.0 Hz, C-2), 29.93 (dd, $^1J_{PC}$ = 30.4 Hz, $^3J_{PC}$ = 15.5 Hz, C-3), 42.85 (d, $^1J_{PC}$ = 24.0 Hz, C-4), 160.00 (s, C-5), 43.70 or 44.50 (s, C-6), 21.30 (s, C-7), 44.50 or 43.70 (s, C-8), 50.40 (s, C-9), 24.50 (s, C-10). ^{13}C NMR data for the aromatic rings (from H−^{13}C HSQC one-bond correlation experiment): Ring A: ^{13}C NMR (500 MHz, CD_2Cl_2):



140.6 (d, $^1J_{PC}$ = 56.4 Hz, C-1), 154.20 (s, C-2), 121.92 (s, C-3), 149.60 (s, C-4), 38.56 (s, C-5), 34.04 (d, $^4J_{PC}$ = 7.1 Hz, C-6), 35.20 (s, C-7), 31.50 (s, C-8). Ring B: ^{13}C NMR (500 MHz, CD_2Cl_2): 132.76 (d, $^1J_{PC}$ = 46.0 Hz, C-1), 159.50 (br, C-2), 122.85 (br, C-3), 150.20 (br, C-4), 39.42 (s, $^3J_{PC}$ = 4.1 Hz, C-5), 34.36 (d, $^4J_{PC}$ = 7.3 Hz, C-6), 34.95 (s, C-7), 31.32 (s, C-8). Note: broad resonances in the B ring indicate some mobility in that area of the molecule. ^{31}P NMR (500 MHz, THF-d_8): δ 248.78 (s, 1P), −15.97 (s, 1P). The structure was determined by X-ray analysis.

Dithiooxo(2,4,6-tri-*tert*-butylphenyl)phosphorane (18). A 0.15 g (0.00049 mol) sample of 1-(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2]-diphosphole (**12**) and 0.016 g (0.00049 mol) of elemental sulfur in 10 mL of toluene were stirred at room temperature for 2 days. It was determined that there was no reaction according to ^{31}P NMR spectral data: the chemical shifts of the starting diphosphole **12** were observed. An additional 0.048 g of the sulfur was added into the reaction mixture, which was then kept at 90 °C for 2 days. The starting signals of diphosphole **12** disappeared and new ^{31}P NMR signals were observed with the dominant downfield signal at 299.50 ppm, which is characteristic of dithiooxophosphoranes (R−P(=S)$_2$). A sample of dithiooxo(2,4,6-tri-*tert*-butylphenyl)-phosphorane was prepared by the literature procedure, and this downfield chemical shift (299.50 ppm) was matched by the two additions of a known sample of dithiooxaphosphorane into the reaction mixture.

Trifluoromethanesulfonate 8-{(2,4,6-Tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidin-1-ium (23) and 1-{3-[2,6-Bis(2,4,6-tri-*tert*-butylphenyl)-[1,2,6]azadiphosphinan-1-yl]propyl}pyrrolidin-2-one (24). A 2.00 g (0.00279 mol) amount of 8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine (**8**), 0.38 g (0.00148 mol) of silver trifluoromethanesulfonate (**20**), and 40 mL of anhydrous methylene chloride were stirred in a nitrogen glovebox for 3 days. The resultant white crystals were filtered off. The yield of trifluoromethanesulfonate 8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)-propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidin-1-ium (**23**) was 1.31 g (54%) with a mp at 214−215 °C (sublimation with decomposition). ^{1}H NMR (500 MHz, CD_3CN, TMS): δ 7.54 (br, 1H), 7.49 (br, 2H), 7.47 (br, 2H), 3.64 (br, 1H), 3.57 (br, 2H), 3.46 (br, 1H), 3.36 (br, 2H), 3.03 (br, 1H), 2.91 (br, 1H), 2.81 (br, 1H), 2.70 (br, 2H), 2.52 (br, 2H), 1.55 (s, 18H, Me), 1.51 (s, 18H, Me), 1.45 (s, 9H, Me), 1.38 (s, 9H, Me), 1.22 (br, 1H, H), 0.03 (br, 1H). ^{31}P NMR (500 MHz, CD_3CN): δ 247.83 (s, 1P, major isomer), 246.57 (s, 1P minor isomer), −15.41 (s, 1P, minor isomer), −13.63 (s, 1P, major isomer, ratio between two isomers is 2:1). The structure was determined by X-ray analysis. The mother liquor from the above recrystallization was purified by chromatography on silica gel with eluent starting from hexane and increasing polarity of eluent to 20% ethyl ether and 80% hexane. The yield of 1-{3-[2,6-bis(2,4,6-tri-*tert*-butylphenyl)-[1,2,6]azadiphosphinan-1-yl]-propyl}pyrrolidin-2-one (**24**) was 0.25 g (23%) with a mp at 172−

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173 °C (sublimation with decomposition). ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 7.34 (s, 2H), 7.27 (s, 2H), 2.85 (br, 2H), 2.75 (br, 2H), 2.10 (br, 2H), 1.90 (br, 2H), 1.80 (br, 2H), 1.70 (br, 2H), 1.60 (s, 18H, Me), 1.45 (s, 18H, Me), 1.40 (br, 2H), 1.35 (br, 2H), 1.20 (s, 18H, Me), 0.45 (br, 2H). ^{31}P NMR (500 MHz, CD_2Cl_2): δ 68.36 (s, 1P). Compound **24** was identified as well by mass spectrometry (ASAP method), which gave an MH^+ ion at 735.55, corresponding to $C_{46}H_{77}N_2P_2$. The structure was determined by X-ray analysis.

8-{(2,4,6-Tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo-[1,2-*a*]pyrimidin-1-ium Bromide (25). A 1.85 g (0.00258 mol) portion of 8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine (**8**), 0.62 g (0.00176 mol) of nickel(II) bromide as a complex with 2-methoxyethyl ether (**21**), and 40 mL of anhydrous methylene chloride were stirred in a nitrogen glovebox for 3 days. The resultant white crystals were filtered off. The yield of 8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidin-1-ium bromide (**25**) was 0.97 g (47%) with a mp at 220 °C (sublimation). ^{1}H NMR (500 MHz, THF-d_8, TMS): δ 12.20 (br, 1H, N−H), 8.05 (br, 1H, H−C═P), 7.40 (s, 2H, H−Ar), 7.50 (s, 2H, H−Ar), 4.40 (br, 1H), 4.10 (br, 2H), 3.20 (br, 1H), 3.15 (br, 2H), 2.95 (br, 1H), 2.90 (br, 1H), 2.40 (br, 1H), 2.30 (br, 2H), 2.00 (br, 2H), 1.55 (s, 18H, Me), 1.50 (s, 18H, Me), 1.35 (s, 9H, Me), 1.30 (s, 9H, Me), 1.40 (br, 1H, H-10), 0.90 (br, 1H). ^{31}P NMR (500 MHz, THF-d_8): δ 249.12 (s, 1P, minor isomer), 248.59 (s, 1P major isomer), −14.91 (s, 1P, major isomer), −16.73 (s, 1P, minor isomer, ratio between two isomers is 9:1). The structure was determined by X-ray analysis.

(Dicarbonyl)[8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine]ruthenium(0) (27). A 0.36 g (0.0005 mol) sample of 8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine (**8**), 0.32 g (0.0005 mol) of ruthenium carbonyl **26**, and 20 mL of anhydrous toluene were refluxed in a nitrogen glovebox for 5 min. Then the reaction mixture was allowed to cool to ambient temperature. The resultant golden crystals were filtered off. The yield of (dicarbonyl)[8-{(2,4,6-tri-*tert*-butylphenyl)-[3-(2,4,6-tri-*tert*-butylphenylphosphanylidene)-propyl]phosphanyl}-2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine]-ruthenium(0) (**27**) was 0.34 g (77%) with a mp at 249 °C (dec). ^{31}P NMR (500 MHz, toluene-d_8): δ 53.77 (d, $^2J_{PP}$ = 36.9 Hz, 1P), 31.79 (d, $^2J_{PP}$ = 36.9 Hz, 1P). See Supporting Information for NMR assignment. The structure was determined by X-ray analysis.

X-ray Diffraction Studies. Data for all structures were collected using a Bruker CCD system at −100 °C. Structure solution and refinement were performed using the SHELXTL[30] set of programs. The Platon-Squeeze[31] program was used to correct the data where the solvent molecules could not be correctly modeled.

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Supporting Information Available: Crystallographic information (CIF file) for complexes **8**, **12**, **23**, **24**, **25**, and **27** and ^{1}H NMR and ^{13}C NMR assignments and the coupling constants for complex **27**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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