A Versatile Approach toward Phosphinine−Phosphole-Based and Phosphinine−Phosphaferrocene-Based Tridentate Ligands

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A synthetic approach toward mixed phosphinine−phosphole and phosphinine−phosphaferrocene tridentate ligands has been studied. In the first step, the metallacycle transfer reaction from 2,5-bis(trimethylsilyl)zirconacyclopentadienes to the corresponding phospholes has been investigated. Three metallacycles **2a**−**c**, bearing different groups at the β-positions of the ring (**a**, R = Ph; **b**, R = *n*-Bu; **c**, R = Me), have been synthesized. Whereas the reaction of PCl_3 with **2a**,**b** respectively leads to 1-P chlorophosphirenes **3a**,**b**, complex **2c** is readily transformed into the corresponding 1-P bromophosphole **4** upon reaction with PBr_3 in dichloromethane. This approach was extended to the synthesis of the bis(dimethylpropynylsilyl)zirconacyclopentadiene compound **5**, which was then further converted into the corresponding 1-P chlorophosphole **6**. Phospholyl anion **7** was obtained from the reaction of **6** with lithium in THF at room temperature. Three 1-R-2,5-bis(dimethylpropynylsilyl)-phospholes (**8a**, R = CH_2CH_2Cl; **8b**, R = CH_2CH_2CN; **8c**, R = $CH_2CH_2CO_2Et$) have been obtained from the reaction of anion **7** with the corresponding species RCH_2CH_2X (X = Cl, Br). The X-ray crystal structure of compound **8b** has been determined. The reaction of anion **7** with $[FeCp(\eta^6\text{-}C_9H_{12})][PF_6]$ and $FeCl_2$ respectively yielded the monophosphaferrocene **9** and the diphosphaferrocene **10**. The X-ray crystal structure of **10** has been determined. The three phosphinine−phosphole tridentate ligands **12a**−**c** have been assembled by reacting phospholes **8a**−**c** with diazaphosphinine **1** followed by reaction of the 2,5-bis(dimethyl(1,2-azaphosphininyl)silyl)phospholes **11a**−**c** with (trimethylsilyl)acetylene in excess. Ligands **12b**,**c** have been converted into the anion **13** upon reaction with LDA at low temperature. The 2,5-bis(dimethyl(phosphininyl)silyl)phosphaferrocene ligand **15**, which was structurally characterized, has been prepared by following the strategy devised for the synthesis of ligands **12**. Reaction of ligands **12a** and **15** with $[Rh(COD)Cl]_2$ gave respectively the corresponding Rh chloride complexes **16** and **17**. Both complexes adopt a square-planar geometry, and complex **17** has been structurally characterized.

Introduction

The elaboration of ligands incorporating sp^2-hybridized phosphorus moieties is an active area of research in phosphorus chemistry. This interest mainly stems from the difference between the electronic properties of these ligands and those of their corresponding nitrogen analogues and classical tertiary phosphines. Thus, whereas the latter display a significant σ-donating ability and a moderate π-accepting ability, P-sp^2-based ligands are essentially strong π-acceptor sites. This particular behavior allows for the synthesis of electron-rich transition-metal complexes. However, the intrinsic kinetic instability of the P=C double-bond system is a major limiting factor which must be taken into account when elaborating ligands or edifices.[1] This limitation accounts for the attention given to aromatic heterocycles in which the P=C bond is thermodynamically stabilized by resonance. Recent developments have shown that molecules such as functionalized phosphaferrocenes[2,3] and phosphinines[1,4,5] show promising perspectives in

(1) (a) *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme Verlag: Stuttgart, Germany, 1990. (b) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, U.K., 1998.

(2) For reviews on the chemistry of phosphaferrocenes, see: (a) Mathey, F. *New J. Chem.* **1987**, *11*, 585. (b) Mathey, F. *Coord. Chem. Rev.* **1994**, *137*, 1.

(3) For the use of phosphaferrocenes in homogeneous catalysis, see: (a) Deschamps, B.; Ricard, L.; Mathey, F. *J. Organomet. Chem.* **1997**, *548*, 17. (b) Ganter, C.; Brassat, L.; Glinsböckel, C.; Ganter, B. *Organometallics* **1997**, *16*, 2862. (c) Ganter, C.; Brassat, L.; Ganter, B. *Chem. Ber./Recl.* **1997**, *130*, 1771. (d) Ganter, C.; Brassat, L.; Ganter, B. *Tetrahedron: Asymmetry* **1997**, *8*, 2607. (e) Ganter, C.; Glinsböckel, C.; Ganter, B. *Eur. J. Inorg. Chem.* **1998**, 1163. (f) Garrett, C. E.; Fu, G. C. *J. Org. Chem.* **1997**, *62*, 4534. (g) Qiao, S.; Hoic, D. A.; Fu, G. C. *Organometallics* **1998**, *17*, 773. (h) Qiao, S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 4168.

(4) For reviews on phosphinine chemistry see: (a) Märkl, G. In ref 1a, p 220. (b) Hewitt, G. G. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: New York, 1996; Vol. 5, p 639. (c) Le Floch, P.; Mathey, F. *Coord. Chem. Rev.* **1998**, *179*, 771.

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Scheme 1

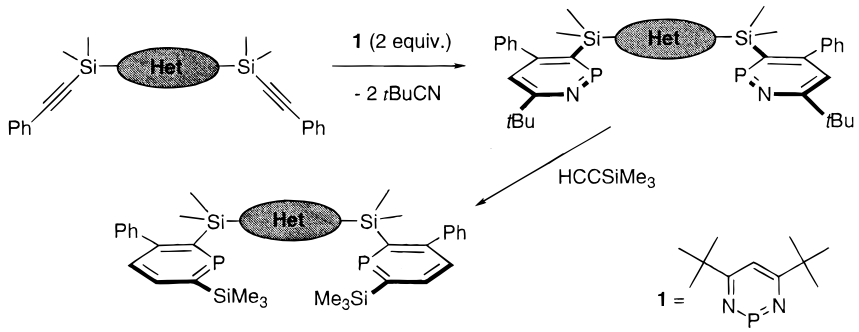
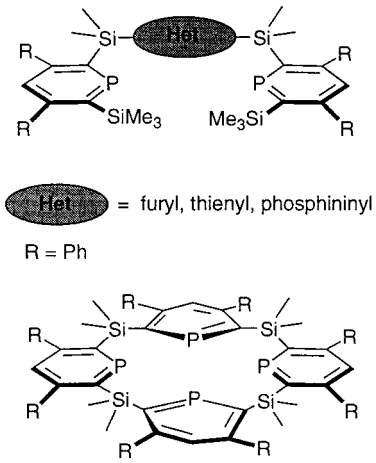


Chart 1



coordination chemistry and homogeneous catalysis. Two years ago, to use phosphinines as building blocks for the synthesis of sophisticated edifices, we devised a new approach to functional derivatives using the reactivity of alkynes toward 1,3,2-diazaphosphinines. This led to the synthesis of phosphinine-based tridentate ligands[6] having a heterocycle as central unit and silacalix[*n*]-phosphinine macrocycles[7] (Chart 1).

As part of a continuing study aimed at expanding the scope of this method, we have focused on the synthesis of mixed phosphinine−phosphole tridentate ligands. The introduction of a phosphole ring as central unit should then lead to other derivatives such as phospholyl anions and phosphametallocenes, thus giving access to a wide range of electronically different tridentate ligands. Herein, we report on these results.

Results and Discussion

Our strategy is similar to that used for the synthesis of tris(phosphinine) ligands. It relies on the synthesis of a bis(dimethylalkynylsilyl)-substituted heterocycle (the central unit) which is then reacted with 2 equiv of diazaphosphinine **1**. In a following step, a second Diels−Alder reaction is carried out, leading to the desired tridentate ligand (Scheme 1).

Extension of this approach to phospholes thus requires the preliminary synthesis of 2,5-bis(dimethylalkynylsilyl)phosphole, an as yet unknown precursor. Although the chemistry of phospholes is particularly well-developed,[8] only two approaches could lead to the synthesis of such a precursor. The first one involves a multistep sequence using 1-phenyl-2,5-dilithiophosphole, a precursor which has been shown to be a convenient source of 2,5-difunctionalized phospholes.[9] The second possible approach relies on metallacycle transfer reactions from zirconacyclopentadienes, a methodology which has been successfully used for the synthesis of various group 14, 15, and 16 heteroles.[10] A determining advantage in favor of this approach is that the nature of the P-substituent can be easily modified. Indeed, as shown by the work of Douglas and Theopold,[10f] the reaction of phosphorus trichloride with zirconacyclopentadienes gives access to 1-chlorophospholes, which can be subsequently transformed into functionalized P derivatives upon nucleophilic substitution. Quite surprisingly, we found that the successful transformation of 2,5-disilyl-substituted zirconacyclopentadienes to the corresponding disilyl-substituted phospholes has never been reported.[11] Ashe and co-workers used these metallacycles as a source of 1,4-disilyl-1,4-diiodobutadienes, which were converted into heteroles via a two-step process which involved the quenching of 1,4-dilithiobutadienes with $RACl_2$ derivatives (A = Bi, Sb, P).[12] To

(5) For the use of phosphinines in homogeneous catalysis, see: (a) Breit, B. *J. Chem. Soc., Chem. Commun.* **1996**, 2071. (b) Breit, B.; Winde, R.; Harms, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2681. (c) Knoch, F.; Kremer, F.; Schmidt, U.; Zenneck, U.; Le Floch, P.; Mathey, F. *Organometallics* **1996**, *25*, 831. (d) Le Floch, P.; Knoch, F.; Kremer, F.; Mathey, F.; Scholz, J.; Scholz, W.; Thiele, K.-H.; Zenneck, U. *Eur. J. Inorg. Chem.* **1998**, 119.

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(8) (a) Quin, L. D. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: New York, 1996; Vol. 5, p 757. (b) Mathey, F. *Chem. Rev.* **1988**, *88*, 429.

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(10) For pertinent articles, including leading references, see: (a) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880. (b) Doxsee, K. M.; Mouser, J. K. M.; Farahi, J. B. *Synlett* **1992**, 13. (c) Breen, T. L.; Stephan, D. W. *Organometallics* **1997**, *16*, 365. (d) Miquel, Y.; Igau, A.; Donnadieu, B.; Majoral, J. P.; Dupuis, L.; Meunier, P. *J. Chem. Soc., Chem. Commun.* **1997**, 279. (e) Zablocka, M.; Igau, A.; Donnadieu, B.; Majoral, J. P.; Skowronska, A.; Meunier, P. *J. Chem. Soc., Chem. Commun.* **1997**, 1239. (f) Douglas, T.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1367. (g) Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696. (h) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.

(11) (a) Ashe mentionned that the reaction of complex **2c** with $PhSbCl_2$ leads to the expected stibole, but not in a satisfactory state of purity; see: Ashe, A. J., III; Kampf, J. W.; Puranik, D. B.; Al-Taweel, S. M. *Organometallics* **1992**, *11*, 2743. (b) While this paper was in the reviewing process, Westerhausen et al. reported that the reaction of **2c** with PCl_3 gave a mixture of 1-chloro- and 1-cyclopentadienylphosphole derivatives: Westerhausen, M.; Digeser, M. H.; Gückel, C.; Nöth, H.; Knizek, J.; Ponkwar, W. *Organometallics* **1999**, *18*, 2491.

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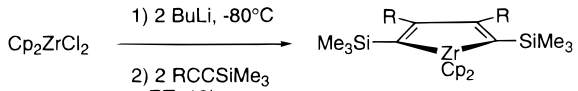
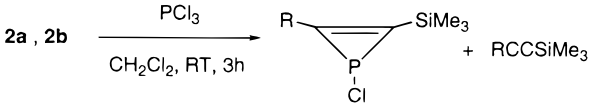
the best of our knowledge, the only available information relative to the transformation of 2,5-disilylzirconacyclopentadienes to heteroles is provided by the work of Tilley et al. In 1998, they reported that the reaction of polymeric dimethylsilyl zirconacyclopentadienes with $PhPCl_2$, S_2Cl_2, and $PhBCl_2$ led to several unidentified products.[13] Furthermore, they showed that similar transformations could not be achieved using the monomeric 2,5-bis(phenyldimethylsilyl)-3,4-dimethylzirconacyclopentadiene. Apparently, the transformation of 2,5-disilyl-substituted zirconacyclopentadienes into the corresponding 2,5-disilylheteroles remains a problem. However, more convincing results have been obtained with monosilyl-substituted zirconacyclopentadienes, as shown by the recent work of Spence et al., who succeeded in the synthesis of a 2-chlorodimethylsilyl-substituted phenylphosphole.[14] As a prerequisite to this study, we reinvestigated the reactivity of bis(silyl)-zirconacyclopentadienes toward halogenophosphines. The three zirconacyclopentadienes **2a**−**c** were thus synthesized by an extension of the original method published by Fagan and Nugent (eq 1).[15]



2a: R =Ph
2b: R = *n*-Bu
2c: R = Me

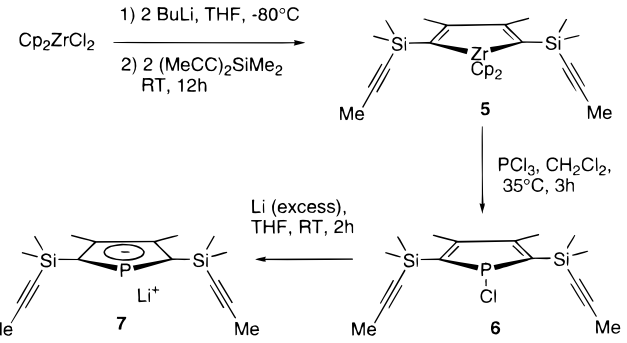
Complexes **2a**,**c** had been synthesized by Erker[16] and Ashe,[12b] respectively. Complex **2b**, previously unknown, was spectroscopically characterized (^1H, ^{13}C, elemental analysis). Metallacycle transfer reactions were attempted using $PhPCl_2$, PCl_3, and PBr_3 in various solvents. Quite surprisingly, the reactivity of **2a**,**b** strongly differs from that of **2c**. Whereas both metallacycles (**2a**,**b**) do not react with $PhPCl_2$, whatever the solvent used, they react with PCl_3 in dichloromethane to give the corresponding 1-chlorophosphirenes **3a,b**, as attested by ^{31}P NMR spectroscopy (δ(**3a** in CH_2Cl_2) −83.4 ppm; δ(**3b** in CH_2Cl_2) −71.3 ppm)[17] (eq 2).



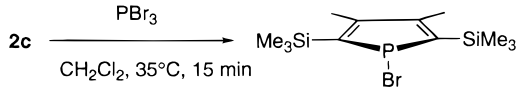
3a: R = Ph
3b: R = *n*-Bu

Phosphirenes **3a,b** have recently been synthesized by us using a metallacycle transfer reaction from the corresponding titanacyclopropene complex.[17] It must be noted that this transformation in the case of zirconium is not totally unprecedented. In 1998, Majoral et al. reported the synthesis of various phosphirenes from P═O-stabilized zirconacyclopropene complexes.[18] Our results confirm a previous observation made by Erker

Scheme 2



concerning the equilibrium between the zirconacyclopentadiene $[ZrCp_2C_4(SiMe_3)_2Ph_2]$ (**2a**) and the bis(alkyne) $[ZrCp_2(\eta^2\text{-}Me_3SiCCPh)_2]$ complexes.[16] A similar equilibrium has been proposed by Tilley et al. to explain polymer-to-macrocycle conversions in the reactions of various diynes with zirconocenes.[19] It seems that the nature of functional groups grafted at the β-positions of zirconium (C_3 and C_4) has a dramatic influence. Thus, in the case of the methyl derivative **2c**, the expected 1-halogenophosphole is readily obtained when CH_2Cl_2 is used as solvent (the use of THF leads to longer reaction times). When PBr_3 is used as reagent, 1-bromophosphole **4** is formed within 15 min at 35 °C (eq 3).



4

Phosphole **4**, which is highly sensitive toward hydrolysis, was not purified and characterized by means of NMR spectroscopy only. Its ^1H and ^{13}C NMR data compare with those recorded for the corresponding 1-phenyl derivative which was recently prepared from the reaction of 2,5-dilithiophosphole with Me_3SiCl.[9]

As a consequence, we set out to synthesize the 2,5-bis(dimethylpropynylsilyl)-3,4-dimethylphosphole derivative. Generation of "zirconocene" followed by treatment with 2 equiv of $MeC{\equiv}CSiMe_2C{\equiv}CMe$ resulted in the formation of an orange solution after 12 h of stirring at room temperature. The formulation of zirconacyclopentadiene **5** was confirmed by ^1H and ^{13}C NMR data (see Scheme 2). As expected, when 2 equiv of diyne was used, the formation of polymers reported by Tilley was not observed. Further support for the structure of complex **5** was provided by the trapping reaction with PCl_3 in CH_2Cl_2. After 3 h of stirring at 35 °C, the ^{31}P NMR of the crude reaction mixture shows the unequivocal formation of the expected 1-chlorophosphole **6**, isolated as a highly moisture-sensitive colorless oil after extraction with dry hexanes (see Scheme 2). All NMR data, which are nearly identical with those recorded for **4**, confirm the proposed structure. Phosphole **6** is a convenient precursor for the synthesis of functional 2,5-

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(16) Erker, G.; Zwettler, R. *J. Organomet. Chem.* **1991**, *409*, 179.
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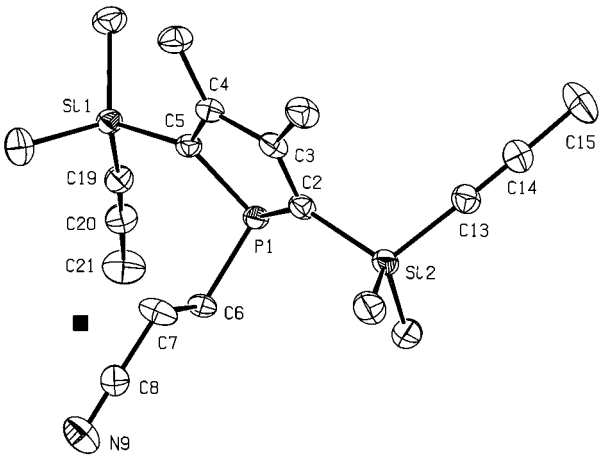

Figure 1. ORTEP drawing of one molecule of **8b**. Hydrogen atoms are omitted for clarity. Ellipsoids are scaled to enclose 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for assignments of the ^{13}C spectrum.

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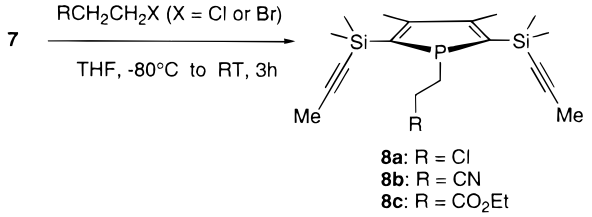
bis(dimethylalkynylsilyl)phospholes and phosphaferrocenes. The conversion of **6** into the corresponding phospholide anion **7** is readily achieved upon reaction with lithium in THF at room temperature, as depicted in Scheme 2.

Anion **7**, only used as an intermediate, was identified by ^{31}P NMR spectroscopy. Interestingly, its resonance (δ(THF) 144.5 ppm) appears to be significantly deshielded with respect to that of the α,α'-unsubstituted species, the 3,4-dimethylphospholide anion (δ(THF) 55.8 ppm).[8a] As already observed in other silyl-substituted sp^2-hybridized phosphorus compounds such as phosphinines, phosphaalkenes, and phosphaalkynes, this phenomenon reflects an increase of s character in the P=C bond, concomitant with a decrease of s character for the lone pair of the phosphorus atom.[20] This would also explain why the magnitudes of ^1J(P−C) coupling constants are relatively large in these disilyl-substituted phospholes (between 30 and 50 Hz, see Experimental Section) compared to other phospholes (usually below 10 Hz). As shown in eq 4, anion **7** is a suitable source of P functionalized phospholes **8**.

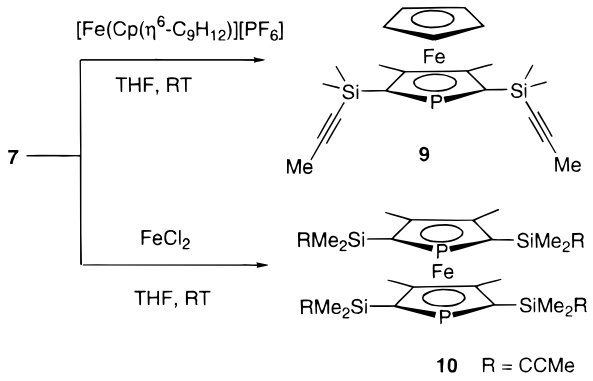


Compounds **8a**−**c** were characterized by NMR techniques and mass spectroscopy and by elemental analysis for **8c**. As previously noted for **7**, ^{31}P NMR chemical shifts of these phospholes are downfield-shifted as a result of the disilyl substitution (between 32.1 and 34.8 ppm). The molecular structure of **8b** was determined by a X-ray diffraction study. An ORTEP view of the molecule is presented in Figure 1 , and significant bond distances and angles values are listed in Table 1. Crystallographic data are listed in Table 5.

Table 1. Significant Bond Lengths (Å) and Angles (deg) for 8b

P(1)−C(2)	1.804(2)	P(1)−C(6)	1.856(2)
C(2)−C(3)	1.363(3)	C(2)−Si(2)	1.867(2)
C(3)−C(4)	1.472(3)	Si(2)−C(13)	1.832(2)
C(4)−C(5)	1.366(3)	C(13)−C(14)	1.202 (2)
C(5)−P(1)	1.791(2)		
Si(2)−C(13)−C(14)	176.9(2)	C(2)−C(3)−C(4)	114.8(2)
C(5)−P(1)−C(2)	93.1(1)	P(1)−C(2)−Si(2)	123.9(1)
P(1)−C(2)−C(3)	108.2(2)	C(2)−Si(2)−C(13)	108.2(1)

The most interesting feature concerns the opening of the internal angle C5−P1−C2 (θ = 93.1(1)°), which is rather large (usually between 89.2 and 91.8°). This increase is consistent with the decrease of s character in the P lone pair as discussed above. A similar statement had been made for classical tertiary phosphines and low-coordinated P compounds.[20] If one ignores this feature, the structure of **8b** deserves no special comment and the other data compare with those reported for other mono- and disubstituted phospholes.[8] Anion **7** was also readily converted into the phosphaferrocene (**9**) or diphosphaferrocene (**10**) derivatives upon treatment with [FeCp(η^6-C_9H_{12})][PF_6] or $FeCl_2$, respectively (eq 5). Both complexes were isolated as red-orange powders after chromatographic purification.



These two complexes are not the first examples of disilyl-substituted phosphaferrocenes. In 1991, Niecke et al. reported the isomerization of an iron bis(methylene)phosphorane complex to a disilylphosphaferrocene,[21] and very recently, Al-Taweel described that of a tetrakis(trimethylsilyl)diphosphaferrocene which has only been characterized by ^1H NMR.[12c] Both complexes **9** and **10** have been identified by conventional NMR techniques, mass spectrometry, and elemental analyses. Diphosphaferrocene **10** has been the subject of an X-ray crystallographic study. An ORTEP view of the molecule is presented in Figure 2 , and the most significant data are listed in Table 2. Crystallographic data are listed in Table 5. The most important feature of this structure concerns the arrangement of the two phospholyl units. Three conformations have been reported for diphosphaferrocenes: C_{2v}, in which the two phosphorus rings are totally eclipsed (α = 0°), C_{2h}, in which the two P atoms point in opposite directions (α = 180°), and finally C_1, in which P atoms are superposed with the β-carbon of

(20) Fluck, E.; Heckmann, G. In *^{31}P NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; Methods in Stereochemical Analysis 8; VCH: Weinheim, Germany, 1987; p 61.

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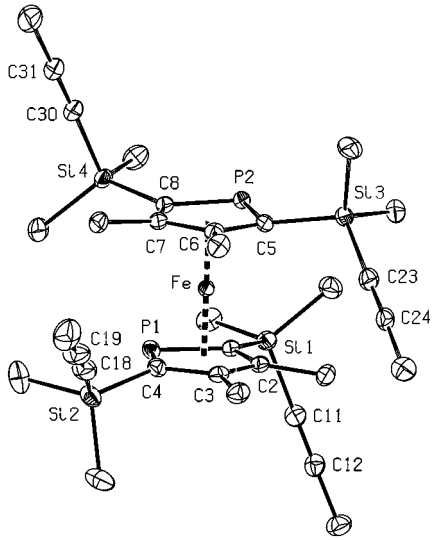


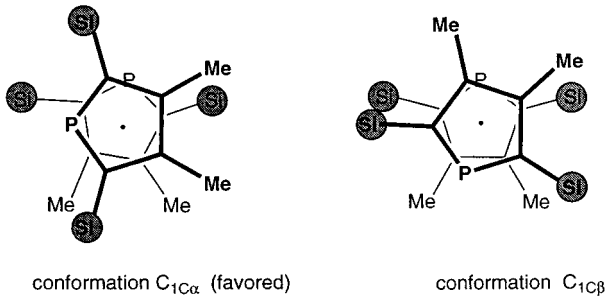
Figure 2. ORTEP drawing of one molecule of **10**. Hydrogen atoms are omitted for clarity. Ellipsoids are scaled to enclose 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for assignments of the ^{13}C spectrum.

Table 2. Significant Bond Lengths (Å) and Angles (deg) for 10

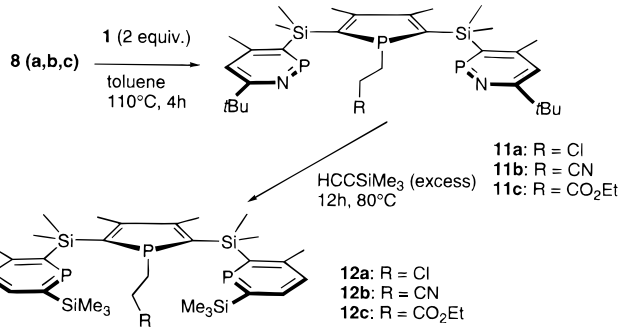
P(1)−C(1)	1.785(2)	C(7)−C(8)	1.426(3)
P(1)−C(4)	1.785(2)	C(5)−Si(3)	1.866(2)
P(2)−C(5)	1.790(2)	Si(3)−C(23)	1.836(2)
P(2)−C(8)	1.786(2)	C(23)−C(24)	1.193(3)
C(5)−C(6)	1.433(3)	Fe−Ct	1.673(3)
C(6)−C(7)	1.427(3)		
C(1)−P(1)−C(4)	91.05(9)	C(7)−C(8)−P(2)	111.4(1)
C(5)−P(2)−C(8)	90.94(8)	P(2)−C(5)−Si(3)	121.2(1)
C(5)−C(6)−C(7)	112.8(2)	C(5)−Si(3)−C(23)	113.12(9)
C(6)−C(7)−C(8)	113.4(2)	Si(3)−C(23)−C(24)	178.4(2)

the other ring ($\alpha = 140-145°$).[22] Calculations on the parent compound $FeC_8H_8P_2$ (Fenske−Hall model[23] and extended Hückel[24]) conclude that the C_1 conformation is the most stable. This assumption was verified for the 3,3′,4,4′-tetramethyl derivative.[25] Interestingly, in the case of the 2,2′,5,5′-tetrakis(trimethylsilyl)diphosphaferrocene, a compound which more closely resembles complex **10** than the tetramethyl species, a similar C_1 ($\theta = 140-145°$) conformation is expected on the basis of ^1H NMR data.[12c] Complex **10** adopts a new type of C_1 conformation which could be named $C_{1C\alpha}$, in which P atoms are not superposed with the β-carbon of the other unit but with the α-carbon ($\alpha = 101°$). This particular geometry very likely results from the steric repulsion between the four alkynyldimethylsilyl groups. Indeed, whereas both conformations imply two interactions between one silyl and one methyl group, the $C_{1C\beta}$ conformation also implies the superposition of the two remaining silyl groups. In the $C_{1C\alpha}$ conformation, this interaction is replaced by an interaction between two methyl groups, explaining why it is favored (see Chart 2). This particular geometry has also been observed in the analogous distibaferrocene[12a] and in the 1,1′-3,3′-tetrakis(trimethylsilyl)ferrocene.[26] Apart from this feature, bond distances and angles are similar to those recorded for mono- and diphosphaferrocenes.

Chart 2



Scheme 3



Having devised an access to 2,5-bis(dimethysilylalkynyl)phospholes and phosphaferrocenes, we then examined the synthesis of phosphinine-based tridentate ligands. All reactions were conducted with the readily available 4,6-di-*tert*-butyl-1,3,2-diazaphosphinine (**1**), which can be prepared from the reaction of the corresponding diazatitanacycle with PCl_3 in the presence of triethylamine.[6,27] In a first step, 1 equiv of phospholes **8a**−**c** was allowed to react with 2 equiv of **1** at 110 °C in toluene to afford bis(azaphosphininyl)phospholes **11a**−**c**, respectively. No attempts have been made to fully characterize these compounds, which were only used as intermediates. Then, further treatment with (trimethylsilyl)acetylene in excess at 80 °C for 12 h gave the desired tridentate ligands **12a**−**c**, which were characterized as slightly oxygen-sensitive pale yellow solids after chromatographic purification (Scheme 3). Their formulations were ascertained by NMR experiments and mass spectrometry and by elemental analyses for **12a,b**.

As previously reported, phospholes bearing CH_2CH_2X (X = CN, CO_2Et) groups at phosphorus are efficient precursors of phospholide anions upon treatment with a base.[28] This reaction can be transposed without any difficulties to ligands **12b**,**c**, despite the presence of the electrophilic P atom of phosphinine. Thus, treatment with LDA at low temperature in THF cleanly afforded the corresponding phospholyl derivative **13**, which was

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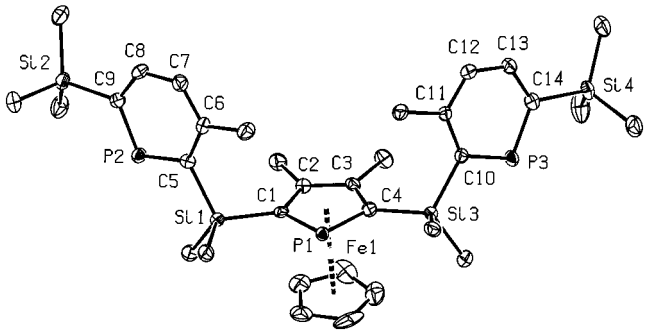
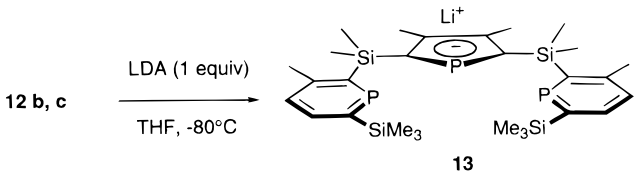
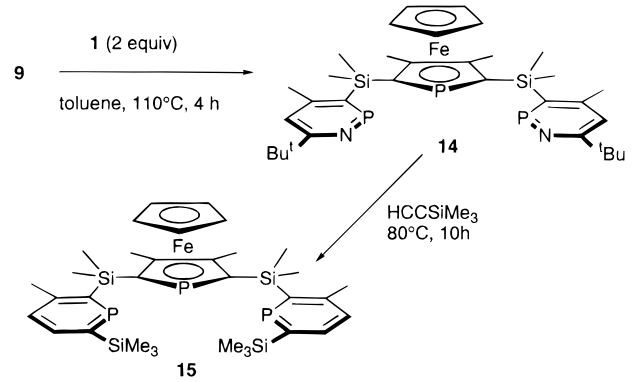


Figure 3. ORTEP drawing of one molecule of **15**. Hydrogen atoms are omitted for clarity. Ellipsoids are scaled to enclose 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for assignments of the ^{13}C spectrum.

only characterized by NMR spectroscopy (^1H, ^{13}C, ^{31}P) due to its high reactivity (eq 6).



We also extended our syntheses to the preparation of the mixed phosphinine−phosphaferrocene tridentate ligand. Although this complex could also be prepared through the reaction of anion **13** with $[FeCp(\eta^6\text{-}C_9H_{12})]^+$, we found the direct condensation of phosphaferrocene **9** with diazaphosphinine **1** to be more convenient, since **9** can be prepared directly from $ZrCp_2Cl_2$ in a two-step sequence. The experimental conditions used are analogous to those described for the synthesis of ligands **12**. Intermediate **14**, which was formed after heating for 4 h at 110 °C in toluene, was reacted with (trimethylsilyl)-acetylene in excess to afford the expected ligand **15** (eq 7).

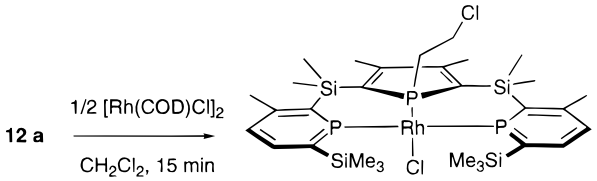


All NMR data, mass spectroscopy, and elemental analyses support the formulation proposed. Ligand **15**, which is the first example of a phosphaferrocene-based tridentate ligand, was also structurally characterized. An ORTEP view of the molecule is presented in Figure 3, and most significant data regarding bond distances and bond angles are listed in Table 3. Crystallographic data are listed in Table 6. The structure of **15** deserves no special comment, all bond distances and angles being nearly comparable to what was observed in isolated

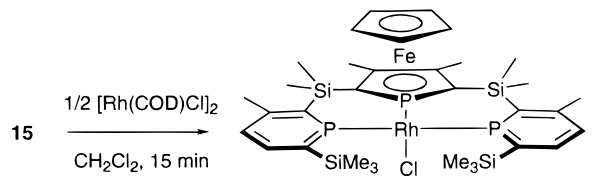
Table 3. Significant Bond Lengths (Å) and Angles (deg) for 15

P(1)−C(1)	1.793(5)	C(5)−P(2)	1.740(5)
C(1)−C(2)	1.421(6)	P(2)−C(9)	1.735(5)
C(2)−C(3)	1.432(6)	C(9)−C(8)	1.387(6)
C(3)−C(4)	1.430(7)	C(8)−C(7)	1.388(6)
C(4)−P(1)	1.785(5)	C(7)−C(6)	1.394(7)
C(1)−Si(1)	1.875(4)	C(6)−C(5)	1.408(6)
Si(1)−C(5)	1.895(5)		
C(4)−P(1)−C(1)	90.8(2)	C(5)−P(2)−C(9)	105.2(2)
P(1)−C(1)−C(2)	11.7(3)	P(2)−C(9)−C(8)	120.6(4)
C(1)−C(2)−C(3)	112.9(4)	C(9)−C(8)−C(7)	124.9(5)
C(2)−C(3)−C(4)	113.1(4)	C(8)−C(7)−C(6)	125.3(4)
C(3)−C(4)−P(1)	111.4(3)	C(7)−C(6)−C(5)	121.6(4)
C(1)−Si(1)−C(5)	110.3(2)	C(6)−C(5)−P(2)	122.4(4)

subunits (phosphinines and phosphaferrocenes). To complete this study, we started a preliminary investigation of the coordinating behavior of ligands **12** and **15**. Their geometry being adapted to the coordination of metals having square-planar environments, we examined their reaction with $[Rh(COD)Cl]_2$. Ligand **12a** cleanly reacts with the rhodium dimer to afford complex **16**, isolated as a slightly oxygen-sensitive red-orange powder (eq 8).



Unfortunately, single crystals suitable for an X-ray study could not be obtained. Nevertheless, interesting information concerning the structure of **16** is provided by the ^{31}P NMR spectrum, which shows an ABMX (X = Rh) spin pattern, indicating that the two phosphinine subunits are not chemically equivalent ($\Delta\delta = 5.75$ ppm). This results very likely from the locked conformation of the two phosphinine rings, in which the trimethylsilyl substituents are directed, respectively, above and below the plane defined by the three phosphorus atoms and the metal center. Indeed, a similar twisted geometry has already been observed in the analogous tris(phosphinine) RhCl complex, which was structurally characterized.[6b] Thus, in the case of **16**, the two phosphinine subunits are differentiated in space by the presence of the substituent at the phosphorus atom of phosphole. The ^{31}P NMR spectrum of **16** was simulated, and every coupling constant has been extracted. Other NMR data (^1H, ^{13}C) and elemental analysis support the formulation proposed. The reaction of ligand **15** with the rhodium dimer affords complex **17**, which was obtained as red-orange microcrystals after purification (eq 9).



All NMR data and elemental analysis confirm the structure proposed for **17**. Similarly to **16**, the two

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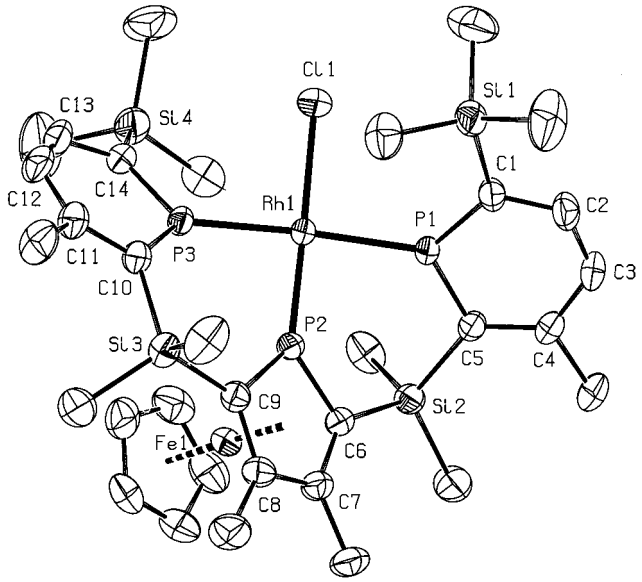

Figure 4. ORTEP drawing of one molecule of **17**. Hydrogen atoms are omitted for clarity. Ellipsoids are scaled to enclose 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for assignments of the ^{13}C spectrum.

Table 4. Significant Bond Lengths (Å) and Angles (deg) for 17

Rh(1)−Cl(1)	2.394(1)	C(9)−P(2)	1.741(4)
P(2)−Rh(1)	2.126(1)	P(1)−C(1)	1.725(4)
P(1)−Rh(1)	2.283(1)	C(1)−C(2)	1.392(6)
P(3)−Rh(1)	2.268(1)	C(2)−C(3)	1.376(6)
P(2)−C(6)	1.742(4)	C(3)−C(4)	1.403(6)
C(6)−C(7)	1.427(5)	C(4)−C(5)	1.412(5)
C(7)−C(8)	1.455(6)	C(5)−P(1)	1.747(4)
C(8)−C(9)	1.433(6)		
P(2)−Rh−P(1)	87.84(3)	P(2)−C(6)−C(7)	109.3(3)
P(1)−Rh(1)−Cl(1)	93.20(4)	C(6)−C(7)−C(8)	113.0(3)
P(2)−Rh(1)−P(3)	87.02(4)	C(7)−C(8)−C(9)	113.0(3)
P(1)−Rh(1)−Cl(1)	93.20(4)	C(8)−C(9)−P(2)	109.0(3)
P(3)−Rh(1)−Cl(1)	92.09(4)	C(5)−P(1)−C(1)	108.4(2)
P(2)−Rh(1)−Cl(1)	178.53(4)	P(1)−C(1)−C(2)	117.5(3)
C(6)−P(2)−C(9)	95.3(2)		

phosphinine subunits are also differentiated in space by the FeCp fragment. However, due to a small chemical shift difference ($\Delta\delta = 0.25$ ppm) for the two phosphinine subunits, the ^{31}P NMR spectrum of **17** only appears as a simplified ABMX spin pattern (first order) and the $^2J(P-P)$ coupling constant through the rhodium center could not be extracted. Additional evidence on the structure of **17** was given by an X-ray crystal structure analysis. An ORTEP drawing of **17** is shown in Figure 4 , and important bond distances and angles are listed in Table 4. Crystallographic data are listed in Table 6. The geometry around the rhodium appears to be perfectly square planar with L−Rh−L angles values between 87.02(4) and 93.20(4)°. The most interesting feature of this structure is given by the arrangement of the ligand. As foreseen on the basis of ^{31}P NMR spectroscopy, the two phosphinine as well as the phosphaferrocene ligands are twisted from the plane bearing the rhodium and defined by the three phosphorus atoms and the chlorine atom. As already noted for the analogous tris(phosphinine) complex, this particular geometry implies that complex **17** is present in the solid state as a racemic mixture of enantiomers which cannot be distinguished because of the centrosymmetrical space group. Except for this geometry, all bond distances and angles are normal and compare to those previously recorded for phosphinine[6b] and phosphaferrocene rhodium(I) complexes.[29]

In summary, we have shown that metathesis from bis(dimethylalkynylsilyl)zirconacyclopentadienes affords an efficient route to the corresponding phospholes, provided that the substituents in the position β to zirconium are methyl groups. A convenient approach to phosphinine-based tridentate ligands having phosphole, phospholide anion, and phosphaferrocene as central units has also been devised. Future efforts will focus on the coordinating behavior of ligands such as **12** and **15** as well as **13**, which could also be used for the synthesis of *ansa* phospholyl−phosphinine complexes.

Experimental Section

General Considerations. All reactions were routinely performed under an inert atmosphere of nitrogen by using Schlenk techniques and dry deoxygenated solvents. Dry hexanes was obtained by distillation from Na/benzophenone and dry CH_2Cl_2 from P_2O_5. Methanol was used as received. Dry Celite was used for filtration. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^1H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants are given in hertz. Mass spectra were obtained at 70 eV with a HP 5989 B spectrometer coupled to a HP 5890 chromatograph by the direct inlet method. The following abreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; v, virtual. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. $(MeCC)_2SiMe_2$[30] and $[Rh(COD)Cl]_2$[31] were prepared according to published procedures.

2,5-Bis(trimethylsilyl)-3,4-dibutyl-1,1-bis(cyclopentadienyl)zirconacyclopentadiene (2b). To a solution of dichlorozirconocene (5.00 g, 17 mmol) in 100 mL of THF at −78 °C was added 2 equiv of *n*-BuLi (22 mL of solution 1.6 M in hexanes). After 30 min of stirring at −78 °C, 2 equiv of 1-(trimethylsilyl)-1-hexyne (5.25 g, 34 mmol) was added with a syringe and the resulting solution was warmed to room temperature. After 15 h the solution was taken to dryness and the compound extracted with hexanes. The solution was then filtered, and complex **2b** was obtained as an orange oil which slowly crystallized after solvent evaporation. Yield: 7.60 g (84%). ^1H NMR ($CDCl_3$): δ 0.06 (s, 12H, $SiMe_2$), 0.90 (s, 6H, Me), 1.23 (m, 8H, 2 × CH_2CH_2), 1.96 (m, 4H, 2 × CH_2), 6.11 (s, 10H, 2 × Cp). ^{13}C NMR ($CDCl_3$): δ 3.45 (s, $SiMe_3$), 14.70 (s, CH_3), 23.85 (s, CH_2), 33.85 (s, CH_2), 38.89 (s, CH_2), 111.20 (s, Cp), 148.53 (s, $C_{3,4}$), 202.07 (s, $C_{2,5}$). MS (CI; *m*/*z* (ion, relative intensity)): 529 (M + H). Anal. Calcd for $C_{28}H_{46}Si_2Zr$: C, 63.45; H, 8.75. Found: C, 63.38; H, 8.68.

2,5-Bis(trimethylsilyl)-3,4-dimethyl-1-bromophosphole (4). Zirconacyclopentadiene **2c** (1.00 g, 2 mmol) was dissolved in 10 mL of CH_2Cl_2 and the solution cooled to 0 °C. PBr_3 (0.19 mL, 2 mmol) was then added to the solution via a microsyringe. The solution was slowly warmed to 35 °C and stirred an additional 15 min. After evaporation of the solvents, phosphole **4** was extracted with dry hexanes. After filtration and removal of the solvent under vacuum, **4** was obtained as a very water sensitive yellow oil. Yield: 0.41 g (61%). ^{31}P NMR ($CDCl_3$): δ 77.60 (s). ^1H NMR ($CDCl_3$): δ 0.30 (s, 12H, $SiMe_3$),

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2.18 (d, 6H, ^4J(H−P) = 6.30, Me). ^{13}C NMR ($CDCl_3$): δ 0.86 (d, ^3J(C−P) = 3.0, $SiMe_3$), 19.06 (d, ^3J(C−P) = 4.25, CH_3), 146.50 (d, ^1J(C−P) = 52.0, $C_{2,5}$), 161.03 (d, ^2J(C−P) = 10.3, $C_{3,4}$). MS (CI; *m*/*z* (ion, relative intensity)): 335−337 (100%, M + H). **4** was too sensitive to give satisfactory elemental analyses.

2,5-Bis(1-propynyldimethylsilyl)-3,4-dimethyl-1,1-bis-(cyclopentadienyl)-zirconacyclopentadiene (5). To a solution of dichlorozirconocene (5.00 g, 17 mmol) in 100 mL of THF at −78 °C was added 2 equiv of *n*-BuLi (22 mL of solution 1.6 M in hexanes). After 30 min of stirring at −78 °C, 2 equiv of diyne (4.65 g, 34 mmol) was added and the solution was stirred at room temperature for 15 h. The volume of volatiles was then reduced, and hexanes was added to precipitate lithium salts. After filtration through Celite, solvents were evaporated, affording **5** as a yellow solid. Yield: 6.20 g (74%). ^{1}H NMR ($CDCl_3$): δ 0.04 (s, 12H, $SiMe_2$), 1.54 (s, 6H, Me), 1.75 (s, 6H, Me), 6.15 (s, 10H, Cp). ^{13}C NMR ($CDCl_3$): δ 2.45 (s, $SiMe_2$), 5.75 (s, C≡C*Me*), 26.25 (s, Me), 87.55 (s, Si*C*≡CMe), 103.15 (s, SiC≡*C*Me), 112.00 (s, Cp), 151.80 (s, $C_{3,4}$), 198.05 (s, $C_{2,5}$). Anal. Calcd for $C_{26}H_{34}Si_2Zr$: C, 63.22; H, 6.94. Found: C, 63.35; H, 7.05.

2,5-Bis(1-propynyldimethylsilyl)-3,4-dimethyl-1-chlorophosphole (6). Zirconacyclopentadiene **5** (6.00 g, 12 mmol) was dissolved in 50 mL of CH_2Cl_2 and the solution cooled to 0 °C. PCl_3 (1.00 mL, 12 mmol) was then added via a syringe. The solution was slowly warmed to room temperature and stirred for an additional 3 h. The resulting mixture was then taken to dryness and the phosphole extracted with dry hexanes. After filtration and removal of the solvent under vacuum, compound **6** was obtained as a very water sensitive yellow oil. Yield: 2.90 g (71%). ^{31}P NMR ($CDCl_3$): δ 77.60 (s). ^{1}H NMR ($CDCl_3$): δ 0.30 (d, 12H, ^4J(H−P) = 5.80, $SiMe_2$), 1.90 (s, 6H, C≡C*Me*), 2.26 (d, 6H, ^4J(H−P) = 6.70, Me). ^{13}C NMR ($CDCl_3$): δ 2.45 (d, ^3J(C−P) = 10.00, $SiMe_2$), 5.25 (s, C≡C*Me*), 18.30 (d, ^3J(C−P) = 2.70, Me), 82.10 (d, ^3J(C−P) = 3.00, Si*C*≡CMe), 105.0 (s, SiC≡*C*Me), 143.60 (d, ^1J(C−P) = 50.40, $C_{2,5}$ of phosphole), 161.45 (d, ^2J(C−P) = 10.80, $C_{3,4}$ of phosphole). MS (CI; *m*/*z* (ion, relative intensity)): 339 (100%, M + H). **6** was too moisture and oxygen sensitive to give satisfactory elemental analyses.

2,5-Bis(1-propynyldimethylsilyl)-3,4-dimethyl-1-(2-chloroethyl)phosphole (8a). To a solution of **6** (1.70 g, 5 mmol) in 30 mL of THF was added lithium in excess (0.10 g, 15 mmol). The resulting solution was stirred at room temperature for 2 h. The formation of anion **7** was monitored by ^{31}P NMR. After removal of the excess lithium, 2 equiv of 1,2-dicholoroethane (0.80 mL, 10 mmol) was added. After 30 min of stirring, volatiles were evaporated and the mixture was purified by chromatography on silica gel, using toluene as eluent. Compound **8a** was obtained as a white solid. Yield: 1.20 g (66%). ^{31}P NMR ($CDCl_3$): δ 32.10. ^{1}H NMR ($CDCl_3$): δ 0.38 (s, 12H, $SiMe_2$), 1.92 (s, 6H, C≡CMe), 2.21 (d, 6H, ^4J(P−H) = 3.90, Me−phosphole), 2.73 (m, 2H, CH_2), 3.04 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 1.35 (d, ^3J(P−C) = 2.60, $SiMe_2$), 5.75 (s, C≡CMe), 19.00 (d, ^3J(P−C) = 5.00, Me of phosphole), 28.00 (d, ^1J(P−C) = 27.20, PCH_2), 42.25 (d, ^2J(P−C) = 8.40, CH_2Cl), 82.95 (d, ^3J(P−C) = 3.20, Si*C*≡CMe), 105.30 (s, SiC≡*C*Me), 139.95 (d, ^1J(P−C) = 29.10, $C_{2,5}$ of phosphole), 159.50 (d, ^2J(P−C) = 10.70, $C_{3,4}$ of phosphole). MS (CI; *m*/*z* (ion, relative intensity)): 366 (M^+). **8a** was too oxygen sensitive to give satisfactory elemental analyses.

2,5-Bis(1-propynyldimethylsilyl)-3,4-dimethyl-1-(2-cyanoethyl)phosphole (8b). To a solution of **6** (2.0 g, 5.9 mmol) in 30 mL of THF was added lithium in excess (0.10 g, 15 mmol). The resulting solution was stirred at room temperature for 2 h. As above, formation of **7** was monitored by ^{31}P NMR. After removal of the excess of lithium, 0.9 equiv of 3-bromopropionitrile (0.44 mL, 5.31 mmol) was added. After the mixture was stirred for 30 min, volatiles were evaporated, and the mixture was purified by chromatography on silica gel using toluene as eluent. Compound **8b** was obtained as a white solid. Crystals were obtained by diffusion of hexanes into a CH_2Cl_2 solution. Yield: 1.60 g (76%). ^{31}P NMR (C_6D_6): δ 34.20. ^{1}H NMR (C_6D_6): δ 0.59 (s, 12H, $SiMe_2$), 1.73 (s, 6H, C≡CMe), 1.88 (m, 2H, CH_2), 2.17 (d, 6H, ^4J(P−H) = 4.00, Me of phosphole), 2.63 (m, 2H, CH_2). ^{13}C NMR (C_6D_6): δ 1.65 (d, ^3J(P−C) = 2.50, $SiMe_2$), 5.30 (s, C≡C*Me*), 13.40 (d, ^2J(P−C) = 2.90, CH_2CN), 19.00 (d, ^3J(P−C) = 5.10, Me of phosphole), 21.05 (d, ^1J(P−C) = 29.10, PCH_2), 83.20 (d, ^3J(P−C) = 2.90, Si*C*≡CMe), 105.85 (s, SiC≡*C*Me), 120.75 (d, ^3J(P−C) = 3.10, CN), 140.75 (d, ^1J(P−C) = 30.60, $C_{2,5}$ of phosphole), 160.60 (d, ^2J(P−C) = 10.60, $C_{3,4}$ of phosphole). MS (CI; *m*/*z* (ion, relative intensity)): 357 (M^+). **8b** was too oxygen sensitive to give satisfactory elemental analyses.

2,5-Bis(1-propynyldimethylsilyl)-3,4-dimethyl-1-(ethyl propionate)phosphole (8c). To a solution of **6** (2.20 g, 6.5 mmol) in 30 mL of THF was added lithium in excess (0.15 g, 22 mmol). The solution was stirred at room temperature for 2 h, and periodic controls allowed us to follow the formation of anion **7**. After removal of the excess lithium, 0.9 equiv of ethyl 3-bromopropionate (0.75 mL, 5.85 mmol) was added. After 30 min of stirring, volatiles were evaporated, and the mixture was purified by chromatography on silica gel using toluene as eluent. Compound **8c** was obtained as a white solid. Yield: 2.10 g (80%). ^{31}P NMR ($CDCl_3$): δ 34.80. ^{1}H NMR ($CDCl_3$): δ 0.36 (s, 12H, $SiMe_2$), 1.20 (t, 3H, ^3J(H−H) = 7.20, Me), 1.80 (m, 2H, PCH_2), 1.89 (s, 6H, C≡CMe), 2.22 (d, 6H, ^4J(P−H) = 3.60), 2.46 (m, 2H, CH_2), 4.05 (q, 2H, ^3J(H−H) = 7.20, CH_2). ^{13}C NMR ($CDCl_3$): δ 1.25 (s, $SiMe_2$), 5.70 (s, C≡C*Me*), 14.85 (s, Me), 19.00 (d, ^3J(P−C) = 5.10, Me of phosphole), 19.25 (d, ^1J(P−C) = 24.20, PCH_2), 30.30 (d, ^2J(P−C) = 4.40, CH_2), 60.90 (s, OCH_2), 83.20 (d, ^3J(P−C) = 2.20, Si*C*≡CMe), 104.95 (s, SiC≡*C*Me), 140.70 (d, ^1J(P−C) = 29.20, $C_{2,5}$ of phosphole), 159.75 (d, ^2J(P−C) = 10.50, $C_{3,4}$ of phosphole), 174.30 (d, ^3J(P−C) = 1.80, CO_2Et). MS (CI; *m*/*z* (ion, relative intensity)): 404 (M^+). Anal. Calcd for $C_{21}H_{33}O_2PSi_2$: C, 62.34; H, 8.22. Found: C, 62.55; H, 8.40.

2,5-Bis(1-propynyldimethylsilyl)-3,4-dimethyl-1-phosphaferrocene (9). To a solution of **6** (2.8 g, 8.3 mmol) in 30 mL of THF was added lithium in excess (0.20 g, 30 mmol). Formation of anion **7** was controlled by ^{31}P NMR. After 2 h, the excess of lithium was removed and 0.9 equiv of [Fe(η^6-$C_6H_5C_3H_7$)(η^5-Cp)]$^+PF_6^-$ (2.92 g, 7.54 mmol) was added. After 30 min of stirring, volatiles were evaporated, and the mixture was purified by chromatography on silica gel using hexanes/dichloromethane (4:1) as eluent. Complex **9** was obtained as an orange solid. Yield: 2.10 g (60%). ^{31}P NMR ($CDCl_3$): δ −23.70. ^{1}H NMR ($CDCl_3$): δ 0.27 (s, 6H, $SiMe_2$), 0.38 (d, 6H, ^4J(P−H) = 2.00, $SiMe_2$), 1.93 (s, 6H, C≡CMe), 2.38 (s, Me of phosphole), 4.30 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$): δ 1.50 (d, ^3J(P−C) = 9.00, $SiMe_2$), 2.15 (d, ^3J(P−C) = 1.60, $SiMe_2$), 5.65 (s, C≡C*Me*), 17.00 (s, Me of phosphole), 73.25 (s, Cp), 82.05 (d, ^1J(P−C) = 79.30, $C_{2,5}$ of phosphole), 84.50 (d, ^3J(P−C) = 4.30, Si*C*≡CMe), 103.30 (d, ^2J(P−C) = 4.50, $C_{3,4}$ of phosphole), 104.35 (s, SiC≡*C*Me). MS (CI; *m*/*z* (ion, relative intensity)): 424 (M^+, 100%). Anal. Calcd for $C_{21}H_{29}FePSi_2$: C, 59.42; H, 6.89. Found: C, 59.68; H, 7.15.

2,2′,5,5′-Tetrakis(1-propynyldimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (10). Lithium in excess (0.1 g, 15 mmol) was added to a solution of **6** (1.0 g, 3.0 mmol) in 20 mL of THF. The mixture was stirred for 2 h. After removal of the excess lithium, 0.45 equiv of $FeCl_2$ (170 mg, 1.35 mmol) was added. After 30 min of stirring, volatiles were evaporated and the mixture was purified by chromatography on silica gel using hexanes/dichloromethane (4:1) as eluent. Complex **10** was obtained as an orange-red solid. Yield: 0.65 g (65%). ^{31}P NMR (CD_2Cl_2): δ −25.70. ^{1}H NMR (CD_2Cl_2): δ 0.42 (br s, 24H, $SiMe_2$), 1.90 (br s, 12H, C≡CMe), 2.35 (d, ^4J(P−C) = 1.80, Me of phospholyl). ^{13}C NMR (CD_2Cl_2): δ 2.15 (br s, $SiMe_2$), 5.20 (s, C≡C*Me*), 15.60 (br m, Me of phospholyl), 84.30 (d, ^3J(P−C) = 4.00, Si*C*≡CMe), 86.00 (br m, $C_{2,5}$ of phospholyl),

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105.00 (br s, $C_{3,4}$ of phospholyl), 105.85 (br s, SiC≡*C*Me). MS (*m*/*z* (ion, relative intensity)): 424 (M^+, 100%). Anal. Calcd for $C_{32}H_{48}FeP_2Si_4$: C, 57.98; H, 7.30. Found: C, 58.33; H, 7.21.

2,5-Bis(2′-(dimethylsilyl)-3′-methyl-6′-(trimethylsilyl)-phosphininyl)-3,4-dimethyl-1-(2-chloroethyl)phosphole (12a). Phosphole **8a** (0.37 g, 1.0 mmol) was dissolved in 10 mL of toluene, and 2 equiv of 1,3,2-diazaphosphinine **1** (2 mmol, in 14 mL of toluene) was added at room temperature. The mixture was heated at 110 °C for 4 h. A control by ^{31}P NMR indicated the complete formation of **11a**. Then 10 equiv of (trimethylsilyl)acetylene (1.40 mL, 10 mmol) was added and the mixture was heated at 80 °C for an additional 10 h. After evaporation of volatiles, the product was purified by chromatography on silica gel using hexanes/CH_2Cl_2 (9:1) as eluent. Ligand **12a** was recovered as a pale yellow solid. Yield: 0.42 g (64%). ^{31}P NMR ($CDCl_3$): δ 29.00 (phosphole), 259.30 (phosphinine). ^{1}H NMR ($CDCl_3$): δ 0.34 (s, 18H, $SiMe_3$), 0.67 (d, 12H, ^4J(P−H) = 1.60, $SiMe_2$), 1.95 (d, 6H, ^4J(P−H) = 3.60, Me of phosphole), 2.20 (m, 2H, PCH_2), 2.48 (d, 6H, ^4J(P−H) = 1.2, Me of phosphinine), 2.95 (m, 2H, CH_2Cl), 7.23 (d, 2H, ^3J(H−H) = 8.00, $H_{4'}$ of phosphinine), 7.97 (dd, 2H, ^3J(P−H) = 9.5, $H_{5'}$ of phosphinine). ^{13}C NMR ($CDCl_3$): δ 0.70 (d, ^3J(P−C) = 5.80, $SiMe_3$), 2.00 (dd, ^3J(P−C) = 4.00, ^3J(P−C) = 12.30, $SiMe_2$), 19.50 (d, ^3J(P−C) = 3.70, Me of phosphole), 27.45 (d, ^3J(P−C) = 5.10, Me of phosphinine), 28.00 (d, ^1J(P−C) = 27.60, P−CH_2), 42.03 (d, ^2J(P−C) = 6.20, CH_2Cl), 130.70 (d, ^3J(P−C) = 24.60, $C_{4'}$ of phosphinine), 139.70 (d, ^2J(P−C) = 11.40, $C_{5'}$ of phosphinine), 141.80 (dd, ^1J(P−C) = 40.70, ^3J(P−C) = 4.60, $C_{2,5}$ of phosphole), 150.15 (d, ^2J(P−C) = 12.40, $C_{3'}$ of phosphinine), 159.80 (d, ^2J(P−C) = 10.30, $C_{3,4}$ of phosphole), 166.85 (d, ^1J(P−C) = 87.70, $C_{2'}$ or $C_{6'}$ of phosphinine), 167.05 (d, ^1J(P−C) = 81.4, $C_{2'}$ or $C_{6'}$ of phosphinine). MS (*m*/*z* (ion, relative intensity)): 650 (M^+). Anal. Calcd for $C_{30}H_{50}ClP_3Si_4$: C, 55.31; H, 7.74. Found: C, 55.48; H, 8.05.

2,5-Bis(2′-(dimethylsilyl)-3′-methyl-6′-(trimethylsilyl)-phosphininyl)-3,4-dimethyl-1-(2-cyanoethyl)phosphole (12b). Phosphole **8b** (0.54 g, 1.5 mmol) was dissolved in 10 mL of toluene, and 2 equiv of 1,3,2-diazaphosphinine (3 mmol) in solution in toluene was added at room temperature. The mixture was then heated to 110 °C for 4 h. After checking for the complete formation of **11b**, 10 equiv of (trimethylsilyl)-acetylene (2.00 mL, 14 mmol) was added and the mixture was further heated at 80 °C for 10 h. After evaporation of solvents, **12b** was purified by chromatography on silica gel with hexanes/CH_2Cl_2 (2:3) as eluent. Ligand **12b** was isolated as a pale yellow solid. Yield: 0.57 g (59%). ^{31}P NMR (C_6D_6): δ 34.00 (phosphole), 261.20 (phosphinine). ^{1}H NMR (C_6D_6): δ 0.39 (s, 18H, $SiMe_3$), 0.65 (br s, 12H, $SiMe_2$), 1.58 (m, 2H, CH_2), 1.78 (d, 6H, ^4J(P−H) = 3.6, Me of phosphole), 1.88 (m, 2H, CH_2), 2.43 (s, 6H, Me of phosphinine), 7.06 (d, 2H, ^3J(H−H) = 8.20, $H_{4'}$ of phosphinine), 7.90 (dd, 2H, ^3J(P−H) = 9.50, $H_{5'}$ of phosphinine). ^{13}C NMR (C_6D_6): δ 0.80 (d, ^3J(P−C) = 6.00, $SiMe_3$), 1.50 (dd, ^3J(P−C) = 3.20, ^3J(P−C) = 8.30, $SiMe_2$), 13.75 (s, CH_2CN), 19.45 (d, ^3J(P−C) = 3.80, Me of phosphole), 20.80 (d, ^1J(P−C) = 29.00, P−CH_2), 27.70 (d, ^3J(P−C) = 6.10, Me of phosphinine), 120.05 (d, ^3J(P−C) = 4.50, CN), 131.30 (d, ^3J(P−C) = 25.30, $C_{4'}$ of phosphinine), 140.30 (d, ^2J(P−C) = 11.40, $C_{5'}$ phosphinine), 142.35 (dd, ^1J(P−C) = 31.20, ^3J(P−C) = 4.50, $C_{2,5}$ of phosphole), 150.40 (d, ^2J(P−C) = 12.20, $C_{3'}$ of phosphinine), 160.95 (d, ^2J(P−C) = 9.90, $C_{3,4}$ of phosphole), 166.85 (d, ^1J(P−C) = 85.60, $C_{2'}$ or $C_{6'}$ of phosphinine), 167.45 (d, ^1J(P−C) = 81.70, $C_{2'}$ or $C_{6'}$ of phosphinine). MS (*m*/*z* (ion, relative intensity)): 641 (M^+), 587 (M − CH_2CH_2CN, 85%). Anal. Calcd for $C_{31}H_{50}NP_3Si_4$: C, 58.00; H, 7.85. Found: C, 58.34; H, 7.88.

2,5-Bis(2′-(dimethylsilyl)-3′-methyl-6′-(trimethylsilyl)-phosphininyl)-3,4-dimethyl-1-(ethyl propionate)phosphole (12c). Phosphole **8c** (0.61 g, 1.50 mmol) was dissolved in 10 mL of toluene, and 2 equiv of 1,3,2-diazaphosphinine (3 mmol) in 20 mL of toluene was added at room temperature. The mixture was heated at 110 °C for 4 h to form the intermediate **11c**. Then 10 equiv of (trimethylsilyl)acetylene (2.00 mL, 14 mmol) was added and the mixture was heated at 80 °C for an additional 10 h. After evaporation of volatiles **12c** was purified by chromatography on silica gel using hexanes/CH_2Cl_2 (2:3) as eluent. Ligand **12c** was recovered as a pale yellow solid.Yield: 0.65 g (63%). ^{31}P NMR ($CDCl_3$): δ 33.90 (phosphole), 261.10 (phosphinine). ^{1}H NMR ($CDCl_3$): δ 0.34 (s, 18H, $SiMe_3$), 0.65 (br s, 12H, $SiMe_2$), 1.22 (t, 3H, ^3J(H−H) = 7.20, Me), 1.85 (m, 2H, PCH_2), 1.91 (d, 6H, ^4J(P−H) = 3.60, Me of phosphole), 2.17 (m, 2H, CH_2), 2.47 (d, 6H, ^4J(P−H) = 1.00, Me of phosphinine), 4.07 (q, 2H, ^3J(H−H) = 7.20, CH_2), 7.22 (d, 2H, ^3J(H−H) = 8.20, $H_{4'}$ of phosphinine), 7.96 (dd, 2H, ^3J(P−H) = 9.30, $H_{5'}$ of phosphinine). ^{13}C NMR ($CDCl_3$): δ 0.65 (d, ^3J(P−C) = 5.90, $SiMe_3$), 1.75 (dd, ^3J(P−C) = 3.80, ^3J(P−C) = 8.40, $SiMe_2$), 14.90 (s, Me), 19.40 (d, ^1J(P−C) = 23.20, PCH_2), 19.45 (dd, ^3J(P−C) = 5.20, ^5J(P−C) = 2.30, Me of phosphole), 27.40 (dd, ^3J(P−C) = 5.80, ^5J(P−C) = 1.70, Me of phosphinine), 30.60 (s, CH_2), 61.00 (s, OCH_2), 130.60 (d, ^3J(P−C) = 24.70, $C_{4'}$ of phosphinine), 139.60 (d, ^2J(P−C) = 11.60, $C_{5'}$ of phosphinine), 142.70 (dd, ^1J(P−C) = 30.90, ^3J(P−C) = 4.80, $C_{2,5}$ of phosphole), 150.15 (d, ^2J(P−C) = 12.30, $C_{3'}$ of phosphinine), 160.00 (d, ^2J(P−C) = 9.60, $C_{3,4}$ of phosphole), 166.85 (d, ^1J(P−C) = 81.90, $C_{2'}$ or $C_{6'}$ of phosphinine), 167.35 (d, ^1J(P−C) = 85.30, $C_{2'}$ or $C_{6'}$ of phosphinine). MS (*m*/*z* (ion, relative intensity)): 688 (M^+). **12c** was too oxygen sensitive to give satisfactory elemental analyses.

[2,5-Bis(2′-(dimethylsilyl)-3′-methyl-6′-(trimethylsilyl)-phosphininyl)-3,4-dimethyl-1-phospholyl]lithium (13). A solution of lithium diethylamide (0.30 mL, 0.5 mol/L in THF) was added to a solution of **12b** (64 mg, 0.1 mmol) in THF (3 mL), at −78 °C. The color rapidly turned to red-brown, and excess base was neutralized by addition of *tert*-butyl chloride (0.10 mL) within 20 s. After evaporation of the volatiles, anion **13** was obtained as a highly oxygen-sensitive red powder. Yield: 45 mg (75%). ^{31}P NMR (THF-d_8): δ 148.30 (phospholyl), 260.10 (phosphinine). ^{1}H NMR (THF-d_8): δ 0.26 (s, 18H, $SiMe_3$), 0.55 (d, 12H, ^4J(P−H) = 0.40, $SiMe_2$), 1.83 (s, 6H, Me of phosphole), 2.41 (d, 6H, ^4J(P−H) = 1.40, Me of phosphinine), 6.99 (d, 2H, ^3J(H−H) = 8.00, $H_{4'}$ of phosphinine), 7.77 (t, 2H, ^3J(P−H) = 8.00, $H_{5'}$ of phosphinine). ^{13}C NMR (THF-d_8): δ 0.10 (d, ^3J(P−C) = 6.00, $SiMe_3$), 3.30 (dd, ^3J(P−C) = 8.70, ^3J(P−C) = 13.20, $SiMe_2$), 17.95 (s, Me of phosphole), 26.50 (s, Me of phosphinine), 130.10 (d, ^3J(P−C) = 25.10, $C_{4'}$ of phosphinine), 135.80 (s, $C_{3,4}$ of phosphole), 137.10 (dd, ^1J(P−C) = 62.40, ^3J(P−C) = 4.00, $C_{2,5}$ of phosphole), 138.25 (d, ^2J(P−C) = 11.30, $C_{5'}$ of phosphinine), 151.00 (d, ^2J(P−C) = 12.40, $C_{3'}$ of phosphinine), 164.25 (d, ^1J(P−C) = 80.50, $C_{2'}$ or $C_{6'}$ of phosphinine), 174.15 (dd, ^1J(P−C) = 89.70, ^3J(P−C) = 2.80, $C_{2'}$ or $C_{6'}$ phosphinine). Anion **13** was too sensitive to give satisfactory elemental analyses.

2,5-Bis(2′-(dimethylsilyl)-3′-methyl-6′-(trimethylsilyl)-phosphininyl)-3,4-dimethyl-1-phosphaferrocene (15). Phosphaferrocene **9** (1.30 g, 3.0 mmol) was dissolved in 20 mL of toluene, and 2 equiv of 1,3,2-diazaphosphinine **1** (6 mmol) in 42 mL of toluene was added at room temperature. The mixture was heated at 110 °C for 4 h to form the intermediate **14**. Then, 10 equiv of (trimethylsilyl)acetylene (4.2 mL, 30 mmol) was added and the resulting mixture was heated at 80 °C for an additional 10 h. After evaporation of solvents, the product was purified on silica gel using hexanes/CH_2Cl_2 (9:1) as eluent. Complex **15** was recovered as an orange solid. Yield: 1.30 g (61%). ^{31}P NMR (C_6D_6): δ −13.70 (phosphaferrocene), 263.00 (phosphinine). ^{1}H NMR (C_6D_6): δ 0.56 (s, 18H, $SiMe_3$), 0.94 (d, 6H, ^4J(P−H) = 1.30, $SiMe_2$), 1.02 (d, 6H, ^4J(P−H) = 3.20, $SiMe_2$), 2.12 (s, 6H, Me of phospholyl), 2.68 (d, 6H, ^4J(P−H) = 1.20, Me of phosphinine), 4.26 (s, 5H, Cp), 7.21 (d, 2H, ^3J(H−H) = 8.10, $H_{4'}$ of phosphinine), 8.04 (dd, 2H, ^3J(P−H) = 9.30, $H_{5'}$ of phosphinine). ^{13}C NMR (C_6D_6): δ 0.85 (d, ^3J(P−C) = 6.00, $SiMe_3$), 3.10 (dd, ^3J(P−C) = 11.30, ^3J(P−C) = 7.00, $SiMe_2$), 3.80 (dd, ^3J(P−C) = 18.20, ^3J(P−C) = 2.60, $SiMe_2$), 18.15 (s, Me of phospholyl), 27.95 (s, Me of phosphinine), 73.00 (s, Cp), 85.70 (dd, ^1J(P−C) = 79.20, ^3J(P−C) = 7.20, $C_{2,5}$ of

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Table 5. Crystallographic Data and Experimental Parameters for 8b and 10

	8b	10
mol formula	$C_{19}H_{26}NPSi_2$	$C_{32}H_{48}Si_4P_2Fe$
mol wt	355.56	662.88
cryst dimens (mm)	0.28 × 0.28 × 0.28	0.32 × 0.28 × 0.28
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	8.5850(10)	13.036(1)
b (Å)	9.3950(10)	13.409(1)
c (Å)	13.640(2)	21.277(2)
α (deg)	80.781(10)	90
β (deg)	81.605(10)	91.05(1)
γ (deg)	78.171(10)	90
V(Å^3)	1055.6(2)	3718.5(9)
Z	2	4
d (g cm^{-3})	1.119	1.18
F(000)	380	1408
μ (cm^{-1})	0.243	0.635
abs cor	none	ψ scans (0.8581−1.0000)
T (K)	123.0(5)	123.0(5)
max θ (deg)	25.87	28.04
no. of rflns measd	4010	9639
no. of indep rflns	3846	9161
R_{int}	0.0183	0.041
no. of rflns used	3464	6802
criterion	$>2\sigma$(I)	$>3.0\sigma$(I)
rfln/param ratio	15	19
wR2	0.1211	0.061
R1	0.0395	0.033
GOF	1.09	1.0
diff peak/hole (e Å^{-3})	0.74(6)−0.65(6)	0.50(6)−0.10(6)

Table 6. Crystallographic Data and Experimental Parameters for 15 and 17

	15	17
mol formula	$C_{33}H_{51}FeP_3Si_4$	$C_{34}H_{53}Cl_3FeP_3RhSi_4$
cryst habit	plate	plate
cryst dimens (mm)	0.14 × 0.12 × 0.03	0.16 × 0.13 × 0.10
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$
a (Å)	10.1710(3)	16.1200(3)
b (Å)	14.2510(8)	12.2990(2)
c (Å)	26.6590(14)	23.0510(4)
α (deg)	90.00	90.00
β (deg)	90.00	101.3380(8)
γ (deg)	90.00	90.00
V (Å^3)	3864.1(3)	4480.90(14)
Z	4	4
d (g cm^{-3})	1.218	1.382
F(000)	1504	1920
μ (cm^{-1})	0.660	1.108
abs cor	none	none
T (K)	125.0(1)	150.0(1)
max θ (deg)	26.37	26.35
no. of rflns measd	4295	9584
no. of indep rflns	4269	9133
R_{int}	0.00	0.00
no. of rflns used	3512	6310
criterion	$>2\sigma$(I)	$>2\sigma$(I)
rfln/param ratio	9	14
wR2	0.0956	0.1141
R1	0.0441	0.0385
Flack param	0.37(2)	not applicable
GOF	1.004	0.941
diff peak/hole (e Å^{-3})	0.389(0.070)/−0.307(0.070)	0.887(0.082)/−0.456(0.082)

phospholyl), 103.50 (d, ^2J(P−C) = 4.50, $C_{3,4}$ of phospholyl), 131.30 (d, ^3J(P−C) = 24.90, $C_{4'}$ of phosphinine), 139.90 (d, ^2J(P−C) = 10.90, $C_{5'}$ of phosphinine), 150.35 (d, ^2J(P−C) = 12.40, $C_{3'}$ of phosphinine), 166.35 (d, ^1J(P−C) = 81.50, $C_{2'}$ or $C_{6'}$ of phosphinine), 168.19 (d, ^1J(P−C) = 87.4, $C_{2'}$ or $C_{6'}$ of phosphinine). MS (*m*/*z* (ion, relative intensity)): 708 (M^+), 643 (M − Cp, 100%). Anal. Calcd for $C_{33}H_{51}FeP_3Si_4$: C, 55.91; H, 7.25. Found: C, 55.45; H, 7.20.

[2,5-Bis(2′-(dimethylsilyl)-6′-(trimethylsilyl)phosphininyl)-3,4-dimethyl-1-(2-chloroethyl)phosphole]rhodium Chloride Complex (16). To a solution of **12a** (80 mg, 0.12 mmol) in 2 mL of dichloromethane was added $^1/_2$ equiv of $[Rh(COD)Cl]_2$ complex (30 mg, 0.06 mmol). The solution instantaneously turned deep red. After evaporation of the volatiles, the residue was washed with hexanes and dried under vacuum, affording **16** as a red-orange powder. Yield: 80 mg (85%). ^{31}P NMR ($CDCl_3$): ABMX system, δ 55.07 (phosphole M, ^1J(P−Rh) = 121.00), 247.80 (phosphinine A, $^2J(P_A-P_M)$ = 76.00, $^2J(P_A-P_B)$ = 465.00, $^1J(P_A-Rh)$ = 162.20), 253.55 (phosphinine B, $^2J(P_B-P_M)$ = 45.00, $^1J(P_B-Rh)$ = 166.00). ^{1}H NMR ($CDCl_3$): δ 0.35 (s, 9H, $SiMe_3$), 0.55 (s, 9H, $SiMe_3$), 0.60 (s, 3H, $SiMe_2$), 0.70 (s, 3H, $SiMe_2$), 0.85 (s, 3H, $SiMe_2$), 0.90 (s, 3H, $SiMe_2$), 2.05 (br s, 3H, Me of phosphole), 2.15 (d, 3H, ^4J(P−H) = 1.30, Me of phosphole), 2.30 (m, 2H, PCH_2), 2.50 (d, 3H, ^4J(P−H) = 1.50, Me of P_A or P_B), 2.59 (d, 3H, ^4J(P−H) = 1.50, Me of P_A or P_B), 2.95 (m, 2H, CH_2Cl), 6.98 (dd, 1H, ^3J(H−H) = 8.40, ^4J(P−H) = 3.90, $H_{4'}$ of P_A or P_B), 7.17 (dd, 1H, ^3J(H−H) = 8.30, ^4J(P−H) = 3.80, $H_{4'}$ of P_A or P_B), 7.86 (m, 2H, $H_{5'}$ of P_A and P_B). ^{13}C NMR ($CDCl_3$): δ 2.55 (m, $SiMe_2$), 2.75 (d, ^3J(P−C) = 3.80, $SiMe_3$), 3.50 (d, ^3J(P−C) = 3.30, $SiMe_3$), 18.70 (m, Me of phosphole), 27.70 (m, Me of P_A and P_B), 36.05 (dd, ^1J(P−C) = 26.00, ^1J(Rh−C) = 8.50, PCH_2), 39.30 (m, CH_2Cl), 127.00 (m, $C_{4'}$ of P_A or P_B), 128.13 (m, $C_{4'}$ of P_A or P_B), 133.65 (d, ^2J(P−C) = 16.50, $C_{2,5}$ of phosphole), 143.46 (d, ^2J(P−C) = 14.70, $C_{5'}$ of P_A or P_B), 144.05 (d, ^2J(P−C) = 14.10, $C_{5'}$ of P_A or P_B), 149.80 (d, ^1J(P−C) = 14.60, $C_{3'}$ of P_A or P_B), 152.60 (d, ^2J(P−C) = 14.00, $C_{3'}$ of P_A or P_B), 155.35 (d, ^2J(P−C) = 11.80, C_3 or C_4 of phosphole), 158.50 (m, $C_{2',6'}$ of P_A and P_B), 160.45 (d, ^2J(P−C) = 9.20, C_3 or C_4 of phosphole). Anal. Calcd for $C_{30}H_{50}Cl_2P_3RhSi_4$: C, 45.62; H, 6.38. Found: C, 45.98; H, 6.32.

[2,5-Bis(2′-(dimethylsilyl)-6′-(trimethylsilyl)phosphininyl)-3,4-dimethyl-1-phosphaferrocene]rhodium Chloride Complex (17). To a solution of phosphaferrocene **15** (100 mg, 0.14 mmol) in 2 mL of dichloromethane was added 0.5 equiv of $[Rh(COD)Cl]_2$ (34 mg, 0.07 mmol). The solution instantaneously turned red-orange. After evaporation of the volatiles, the residue was washed with hexanes and dried under vacuum, affording **17** as an orange powder. Crystals were obtained by diffusion of hexanes into a CH_2Cl_2 solution of **17**. Yield: 95 mg (81%). ^{31}P NMR ($CDCl_3$): ABMX system, δ 74.90 (phosphaferrocene M, ^1J(P−Rh) = 160.0), 242.00 (phosphinine A, $^2J(P_A-P_M)$ = 88.0, $^1J(P_A-Rh)$ = 155.0), 242.20 (phosphinine B, $^2J(P_B-P_M)$ = 88.00, $^1J(P_B-Rh)$ = 155.00). ^{1}H NMR (CD_2Cl_2): δ 0.60 (br m, 30H, $SiMe_3$ and $SiMe_2$), 2.26 (br s, 6H, Me of phospholyl), 2.59 (br s, 6H, Me of P_A and P_B), 4.02 (s, 5H, Cp), 7.12 (m, 2H, $H_{4'}$ of P_A and P_B), 7.85 (m, 2H, $H_{5'}$ of P_A and P_B). ^{13}C NMR (CD_2Cl_2): δ 2.45 (br s, $SiMe_3$), 3.00 (br m, $SiMe_2$), 16.65 (br s, Me of phospholyl), 28.25 (s, Me of P_A and P_B), 73.94 (m, $C_{2,5}$ of phospholyl), 74.25 (s, Cp), 96.75 (d, ^2J(P−C) = 6.60, $C_{3,4}$ of phospholyl), 127.22 (br m, $C_{4'}$ of P_A and P_B), 142.60 (br s, $C_{5'}$ of P_A and P_B), 152.30 (br m, $C_{3'}$ of P_A and P_B), 157.10 (br m, $C_{2'}$ and $C_{6'}$ of P_A and P_B). Anal. Calcd for $C_{33}H_{51}ClFeP_3RhSi_4$: C, 46.78; H, 6.07. Found: C, 46.97; H, 6.19.

X-ray Structure Determinations. All data were collected using Mo Kα (λ = 0.710 73 Å) radiation and a graphite monochromator. For compounds **8b** and **10**, data were measured on an Enraf-Nonius CAD4 diffractometer. The crystal structures were solved and refined using the Nonius MOLEN package. Crystal data are assembled in Table 5. For compounds **15** and **17**, data collection was performed with a Nonius KappaCCD diffractometer. The crystal structures were solved using maXus. While initial refinement was performed with the latter, final least squares was conducted with Shelxl97.[32]

(32) Sheldrick, G. M. SHELXL-97; Universität Göttingen, Göttingen, Germany, 1997.

Illustrations were made using Platon.[33] Crystal data are assembled in Table 6.

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(33) Spek, A. L. Platon, a Multipurpose Crystallographic Tool; Utrecht University, Utrecht, The Netherlands, 1999.

Supporting Information Available: Listings containing atomic coordinates and equivalent isotropic parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen coordinates for structures of compounds **8b**, **10**, **15**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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