$1\sigma^4,2\sigma^x$-Diphosphetes ($x = 2-6$): On the Persistence of the P−P Bond

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Received June 3, 1997[⊗]

Abstract: Irradiation of [bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane at 254 nm in the presence of *tert*-butylphosphaalkyne leads to $1\sigma^4,2\sigma^2$-diphosphete **1** in 90% yield. Derivative **1** reacts with $Fe_2(CO)_9$ and $W(CO)_5(THF)$ giving rise to the corresponding η^1-complexes **2** (48% yield) and **3** (75% yield), respectively. When 1 equiv of methyl trifluoromethanesulfonate and elemental selenium is added to derivative **1**, the cationic and neutral $1\sigma^4,2\sigma^3$-diphosphetes **4** and **5** are isolated in 95 and 66% yields, respectively. Addition of 2 equiv of elemental selenium and bis(trimethylsilyl)peroxide to diphosphete **1** gave rise to $1\sigma^4,2\sigma^4$-diphosphetes **6** (43% yield) and **7** (84% yield), respectively. η^1-($1\sigma^4,2\sigma^2$-Diphosphete)tungsten complex **3** reacted with bis(trimethylsilyl)peroxide affording heterocyclic complex **8** (68% yield). Addition of 1 equiv of tetrachloro-*o*-benzoquinone (TCBQ) to the cationic $1\sigma^4,2\sigma^3$-diphosphete **4** and of 2 equiv to the $1\sigma^4,2\sigma^2$-diphosphete **1** affords the $1\sigma^4,2\sigma^5$- and $1\sigma^4,2\sigma^6$-diphosphetes **9** (86% yield) and **10** (92% yield), respectively. Addition of TCBQ to the η^1-($1\sigma^4,2\sigma^2$-diphosphete)-tungsten complex **3** affords the η^1-($1\sigma^4,2\sigma^4$-diphosphete)complex **11** (88% yield), which reacts with 2 equiv of trimethylphosphine leading to the zwitterionic $1\sigma^4,2\sigma^3$-diphosphete **12** (46% yield). Cleavage of the Si−C bond of complex **3** with 1 equiv of tetrabutylammonium fluoride hydrate gives η^1-($1\sigma^4,2\sigma^2$-diphosphete)complex **13** (61% yield), which reacts with TCBQ leading to the *cis*-1,2-diphosphino alkene complex **14** (77% yield). These results demonstrate that the unsaturated four-membered ring skeleton is a remarkable template for inducing unusual P−P interactions. However, the presence of two very bulky substituents on the ethylenic moiety is necessary for the persistence of the cyclic structure, when the two phosphorus atoms feature a high coordination state. Single crystal X-ray diffraction studies of derivatives **7** and **11**−**14** have been carried out.

Introduction

Although a few stable substituted cyclobutadienes **A**[1] and azetes **B**[2] are known, so far the corresponding σ^2-phosphetes **C′** and σ^2,σ^2-diphosphetes **C″** have only been identified as ligands in transition metal complexes.[3] In contrast to the antiaromatic derivatives **C**, σ^4-phosphetes **D** are stable species:[4] the R_2P moiety interrupts the conjugation of the four-π electrons system, and derivatives **D** are best described by the zwitterionic structure **D′**. It is thus clear that the stability of four-π electron four-membered rings featuring phosphorus centers is strongly dependent on the coordination number of the phosphorus atoms. Note that two types of mixed-valent phosphorus four-π electron four-membered heterocycles **E**[5a] and **F**[5b] have very recently been described. Due to the presence of two σ^4-phosphorus atoms, they possess a bis(ylidic) structure **G** that diphosphetes **D** cannot adopt.

A few stable phosphanylidene-σ^4-phosphoranes **H** are known.[6] Among other resonance forms, **H** can be regarded as **H′**, a phosphine complex of a phosphinidene unit. Since phosphinidenes feature a phosphorus atom with the lowest possible coordination number, they are the ideal precursors for building phosphorus derivatives with different coordination states.

In this paper, we describe the synthesis of 1,2-diphosphetes **I** featuring a σ^4- and a σ^x-phosphorus atom ($x = 2-6$),[7] and

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

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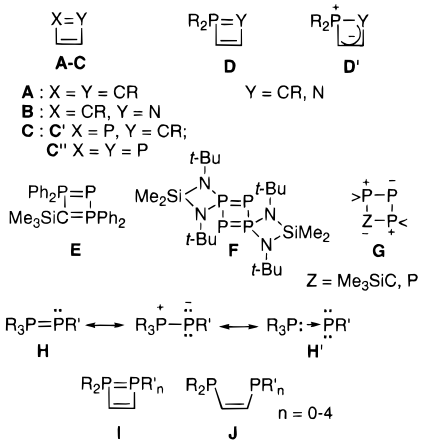
S0002-7863(97)01821-0 CCC: $14.00

Table 1. Comparison of Selected NMR Data for Compounds **1**−**14** at 298 K[a]

	δ N_2P	δ *P*	*J*(P,P)	^3J(*P*NC*H*)	^2J(*P*NC*H*)	δCSiMe$_3$ ($J_{P,C}$)	δ *C*tBu ($J_{P,C}$)
1	+49.2	+58.4	201.2	13.6	5.6	105.7 (36.8; 4.2)	224.3 (54.9; 9.9)
2	+57.4	+112.6	205.5	13.4	5.6	134.7 (31.1; 13.5)	214.0 (51.8; 2.2)
3	+57.4	+41.7	175.4	13.4	5.2	126.1 (34.9; 14.2)	209.7 (39.2; 7.1)
4	+40.2	+54.9	107.4	10.9	5.2−4.8	151.7 (36.6; 9.5)	193.7 (23.0; 0)
5	+39.2	+117.1	246.4	10.5−7.8	4.0−2.7	158.5 (28.5; 12.5)	202.4 (51.8; 15.3)
6	+59.2	+83.2	47.1	10.0	3.0	135.5 (25.6; 18.3)	194.9 (53.3; 22.6)
7	+114.1	+44.5	6.7	13.3	4.2	141.0 (28.3; 20.4)	199.9 (105.3; 78.7)
8	+72.4	+160.8	110.9	10.9	6.4−3.9	144.6 (13.1; 7.4)	201.4 (48.0; 1.8)
9	+117.0	+25.2	35.8	10.0−13.6	8.0−3.6	142.2 (44.2; 26.5)	209.9 (85.0; 7.6)
10	+131.3	-65.4	122.1	9.0	4.3−4.5	130.5 (39.2; 13.9)	207.0 (120.4; 89.1)
11	+80.4	+74.3	25.1	12.3	8.7	130.0 (40.4, 27.0)	215.4 (73.6−41.9)
12[b]	+54.2	+164.5	200.8	21.9		152.1 (32.2, 12.7)	198.4 (28.4; 15.3)
13	+45.2	+68.2	220.4	16.1	4.5	111.2 (72.6; 17.8)[c]	193.7 (42.6; 17.3)
14	+38.9	+224.5	24.5	11.2	9.7	142.0 (20.8; 8.5)[c]	154.2 (28.7)

[a] Chemical shifts in parts per million and coupling constants in Hertz. [b] $T = 183$ K. [c] Chemical shift of the ethylenic CH group.

Scheme 1

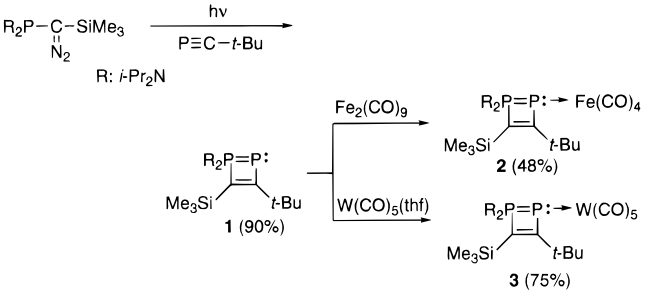


we discuss the persistence of the P−P bond in such derivatives. Indeed, due to ring strain, it might be expected that most of the compounds **I** exist as 1,2-diphosphorus substituted alkenes **J**. Here we analyze the factors favoring cyclic structures **I** over their open chain counterparts **J** (Scheme 1).

Results

Irradiation of [bis(diisopropylamino)phosphino](trimethylsilyl)-diazomethane[8] at 254 nm in the presence of *tert*-butylphosphaalkyne[9] led to $1\sigma^4,2\sigma^2$-diphosphete **1**, which was isolated as a yellow oil in 90% yield. Addition of $Fe_2(CO)_9$ and $W(CO)_5$(THF) afforded the corresponding complexes **2** (48% yield) and **3** (75% yield), respectively (Scheme 2). The best indications of the cyclic structure are the small $^2J_{PNCH}$ coupling constants (5.2−5.6 Hz) typical for diisopropylamino-substituted σ^4-phosphorus atoms ($^2J_{PNCH}$: σ^4-P, 2−8 Hz; σ^3-P, 7−15 Hz)[10] and the very low-field position of the ^{13}C NMR signal of the sp^2-hybridized *C*-tBu carbon atom (209.7−224.3 ppm)[11] (Table 1). The cyclic structure is also supported by the multiplicity of the equatorial carbonyl ligands of the organometallic fragments [**2**: 216.5, dd, $J_{PC} = 7.8$ and 3.8 Hz; **3**: 198.9, dd, $J_{PC} = 3.4$ and 3.4 Hz]. Note that the value of the J_{PP} coupling constant is not relevant to the discussion since it results from superimposition of the ^1J and ^3J coupling constants. Moreover, several examples of large through space PP coupling constants have been observed in the case of *cis*-diphosphorus substituted alkene or benzene derivatives.[13] Finally, a single-crystal X-ray diffraction study performed on the (η^1-diphosphete)pentacarbonyltungsten complex **3**,[7a] definitively proved the cyclic structure (Table 2).

Scheme 2



Compound **1** reacted with 1 equiv of methyl trifluoromethanesulfonate and elemental selenium affording the cationic and neutral $1\sigma^4,2\sigma^3$-diphosphetes **4** and **5**, in 95 and 66% yields, respectively. Addition of 2 equiv of elemental selenium and bis(trimethylsilyl)peroxide to diphosphete **1** gave rise to $1\sigma^4,2\sigma^4$-diphosphetes **6** (43% yield) and **7** (84% yield), respectively (Scheme 3). Here also, the small $^2J_{PNCH}$ coupling constant (3.0−5.2 Hz) and the low-field ^{13}C NMR chemical shift of the *C*-tBu carbon atom (193.7−202.4 ppm) (Table 1) are typical for the four-membered cyclic structure. Furthermore, note the multiplicity of the NMR signals of the methyl group of **4** [^{1}H NMR: 1.8, dd, $J_{PH} = 4.9$ and 19.1 Hz; ^{13}C NMR: 11.3, dd, $J_{PC} = 42.0$ and 8.5 Hz]. The main difference between the spectroscopic data for selenoxophosphine **5** and diselenoxophosphorane **6** lies in the ^{77}Se NMR (**5**: −63.0, $^1J_{PSe} = 487$

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Table 2. Comparison of Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds **3**, **7**, and **10**−**14**

	3	**7**	**10**	**11**	**12**	**13**	**14**
P1−P2	2.176(3)	2.259(2)	2.296(1)	2.228(3)	2.210(1)	2.201(3)	*b*
P2−C2	1.842(7)	1.827(6)	1.921(2)	1.904(7)	1.861(2)	1.847(8)	1.829(4)
C2−C1	1.391(10)	1.380(8)	1.355(3)	1.362(12)	1.367(3)	1.359(12)	1.336(6)
C1−P1	1.804(7)	1.831(5)	1.823(2)	1.811(7)	1.801(2)	1.786(8)	1.835(4)
P1−N1	1.664(6)	1.665(4)	1.677(2)	1.666(9)	1.644(2)	1.668(7)	1.694(4)
P1−N2	1.651(6)	1.648(4)	1.660(2)	1.639(7)	1.653(2)	1.639(6)	1.699(4)
C1−Si	1.892(7)	1.906(6)	1.916(2)	1.912(9)	1.916(2)		
C2−C3	1.525(10)	1.520(8)	1.538(3)	1.530(10)	1.528(3)	1.521(11)	1.561(6)
P2−W	2.623(2)			2.608(3)		2.569(2)	2.415(1)
P2−O1		1.487(4)	1.735(2)	1.693(6)	1.673(2)		1.689(3)
P2−O2		1.483(4)	1.762(1)	2.017(6)	*a*		1.681(3)
P2−O3			1.715(1)				
P2−O4			1.753(1)				
P1−C1−C2	95.1(5)	99.7(4)	101.4(2)	97.9(5)	97.7(2)	97.5(6)	129.6(4)
C1−C2−P2	109.6(5)	107.6(4)		104.7(5)	107.6(2)	108.8(6)	118.6(3)
C2−P2−P1	71.9(3)	73.6(2)		70.9(2)	71.8(1)	71.5(3)	
P2−P1−C1	83.1(2)	78.2(2)	79.7(1)	79.6(3)	80.9(1)	81.5(3)	
N1−P1−P2	125.0(2)	119.0(2)	121.9(1)	114.8(3)	118.3(1)	126.2(3)	
N1−P1−C1	110.8(3)	113.1(2)	112.9(1)	108.6(4)	110.7(1)	109.6(4)	99.6(2)
N1−P1−N2	106.0(3)	106.7(2)	108.5(1)	108.8(4)	110.1(1)	106.8(3)	109.5(2)
N2−P1−P2	111.9(3)	121.2(2)	116.6(1)	119.2(3)	115.0(1)	112.9(3)	
N2−P1−C1	119.6(3)	116.5(2)	114.7(1)	123.3(4)	119.5(1)	118.7(4)	98.5(2)
P1−P2−W	129.2(1)			131.3(1)		126.9(1)	
W−P2−C2	129.7(3)			108.8(3)		129.0(3)	122.8(1)
P2−C2−C3	119.9(6)	102.2(5)	123.3(2)	128.3(6)	121.6(2)	124.6(7)	119.5(3)
C3−C2−C1	130.3(7)	132.2(5)	129.2(2)	127.1(6)	130.8(2)	126.3(8)	121.6(4)
C2−C1−Si	134.6(6)	131.4(4)	136.1(2)	136.9(6)	134.8(2)		
Si−C1−P1	130.3(4)	128.9(3)	122.5(1)	125.2(5)	127.5(1)		
P1−P2−O1		106.0(2)	96.7(1)	116.5(2)	109.6(1)		
P1−P2−O2		120.2(2)	94.3(1)	85.4(3)			
P1−P2−O3			173.1(1)				
P1−P2−O4			89.9(1)				
O1−P2−O2		121.2(2)	89.1(1)	84.2(3)			93.1(2)
O1−P2−O3			85.4(1)				
O1−P2−O4			173.0(1)				
O2−P2−O3			92.3(1)				
O2−P2−O4			88.1(1)				
O3−P2−O4			88.3(1)				
C2−P2−O1		111.7(2)	90.1(1)	95.0(3)	94.5(1)		105.2(2)
C2−P2−O2		114.6(2)	165.4(1)	153.1(3)			103.2(2)
C2−P2−O3			102.1(1)				
C2−P2−O4			94.2(1)				

[a] d(P2−O2) = 2.328(2). [b] d(P2−P1) = 3.389(4).

Hz; **6**: +264.8, $^1J_{PSe}$ = 699 Hz). For compound **7**, the value of the J_{PP} coupling constant is extremely small (6.7 Hz); however, the cyclic structure has been confirmed by a single-crystal X-ray diffraction study (Tables 2 and 3, Figure 1). This is a nice demonstration that the J_{PP} value is not a conclusive proof of a cyclic structure.

η^1-(1σ^4,2σ^2-Diphosphete)tungsten complex **3** reacted with bis(trimethylsilyl)peroxide affording heterocyclic complex **8** (68% yield). In addition to the NMR arguments already used to endorse the cyclic structure of compounds **1**−**7**, note that as observed for complex **3**, the equatorial carbonyl ligands of derivative **8** appeared as doublet of doublets (198.4, dd, J_{PC} = 7.3 and 1.1 Hz) (Table 1).

Addition of 1 equiv of tetrachloro-*o*-benzoquinone (TCBQ) to the cationic 1σ^4,2σ^3-diphosphete **4** and of 2 equiv to the 1σ^4,2σ^2-diphosphete **1** cleanly afforded the 1σ^4,2σ^5- and 1σ^4,2σ^6-diphosphetes **9** (86% yield) and **10** (92% yield), respectively (Scheme 3). A strong indication of the P−P bond in these compounds is given by the low-field ^{31}P NMR chemical shift of the amino-substituted phosphorus atom (**9**: +117.0; **10**: +131.3), which is inconsistent with a free phosphine.[10] The cyclic structure has been confirmed by a single-crystal X-ray diffraction study of compound **10** (Table 2).[7b]

Addition of TCBQ to the η^1-(1σ^4,2σ^2-diphosphete)tungsten complex **3** afforded complex **11** (88% yield) (Scheme 4), which has also been subjected to a single-crystal X-ray diffraction study (Table 2, Figure 2). Treatment of complex **11** with 2 equiv of trimethylphosphine afforded derivative **12**, which was isolated after recrystallization as pale yellow crystals in 46% yield (Scheme 4). The NMR spectra for compound **12** were temperature-dependent, indicating that a dynamic process was taking place. At room temperature, the ^{31}P NMR spectrum shows an AX system (+62.0, +138.6, J_{PP} = 213.9 Hz). In comparison with complex **11**, the phosphorus atom bound to TCBQ is notably deshielded ($\Delta\delta$ = 64 ppm). This datum precludes the zwitterionic structure **12′**, since negatively charged σ^4,λ^4-phosphorus atoms (phosphoranides) show high-field chemical shifts.[14] In the ^{13}C NMR spectrum, the signals of the endocyclic carbon atoms and of the aromatic ring were not observed. Interestingly, the $^2J_{PNCH}$ coupling constants are small (4.3−5.4 Hz) indicating the presence of a σ^4-phosphorus and thus that **12** is a four-membered ring. Cooling the sample down resulted in a significant deshielding of the phosphorus atom bound to TCBQ up to $\Delta\delta$ = 26 ppm at 183 K; the other phosphorus atom being less perturbed ($\Delta\delta$ = 8 ppm). At 183 K, the ^{13}C NMR signals of the endocyclic carbon atoms appeared at 152.1 (J_{PC} = 12.7 and 32.2 Hz, *C*SiMe$_3$) and 198.4 (J_{PC} = 15.3 and

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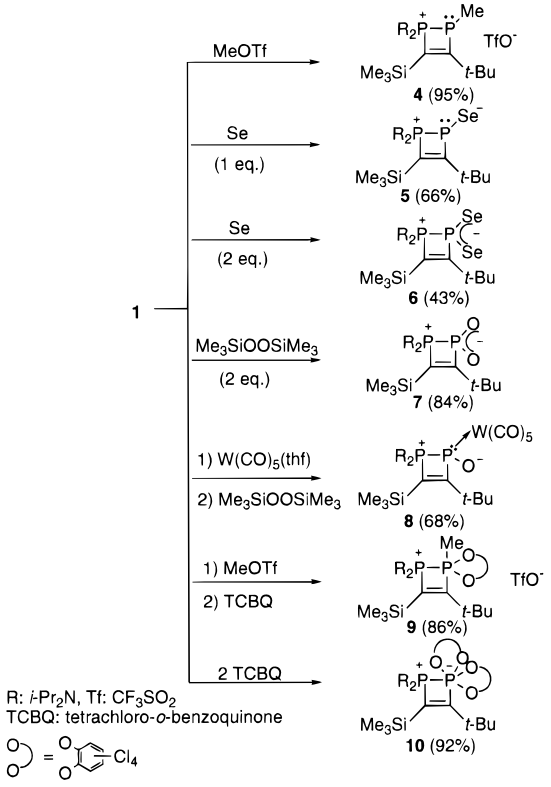
Table 3. Crystallographic Data for Compounds **7** and **11**−**14**

	7	**11**	**12**	**13**	**14**
chem formula	$C_{21}H_{46}N_2O_2P_2Si$	$C_{33}H_{48}Cl_6N_2O_7P_2SiW$	$C_{27}H_{46}Cl_4N_2O_2P_2Si$	$C_{23}H_{38}N_2O_5P_2W$	$C_{29}H_{38}Cl_4N_2O_7P_2W$
fw	448.63	1071.31	662.49	668.34	914.20
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a, Å	10.874(4)	21.767(3)	11.195(1)	10.031(2)	9.794(2)
b, Å	15.973(4)	20.248(2)	16.323(3)	21.365(4)	20.319(4)
c, Å	15.478(4)	20.577(3)	18.764(2)	13.833(3)	19.380(4)
β, deg	97.99(3)	97.78(1)	94.03(1)	99.58(3)	101.45(3)
V, Å^3	2662.3(14)	8986.0(20)	3420.4(8)	2923.2(10)	3779.9(13)
F(000)	984	4288	1400	1336	1816
Z	4	8	4	4	4
D_{calc}, g cm^{-3}	1.119	1.584	1.287	1.519	1.606
μ (Mo Kα), mm^{-1}	0.226	3.069	0.501	4.093	3.466
$T_{min} - T_{max}$		0.6678−0.9998			
2θ range, deg	5−43	3−44	4−49	4−47	4−46
no. of data collected	2955	11354	22062	4197	5080
no. of unique data	2950	10995	5239	4187	5073
R_{av} (on I)		0.0443	0.0358		
no. of params varied	266	877	352	309	421
S	0.701	0.878	1.036	0.942	0.788
R	0.057	0.0417	0.0428	0.0488	0.0250
R_w	0.1142	0.0993	0.1205	0.1070	0.0520
$(\Delta/\rho)_{max}$	0.208	0.891	0.288	1.586	0.879
$(\Delta/\rho)_{min}$, eÅ^{-3}	−0.229	−0.976	−0.280	−0.867	−0.777

Scheme 3



28.4 Hz, *C*t-Bu), strongly suggesting a four-membered ring structure. Note that the $^2J_{PNCH}$ coupling constants were not observable due to the width of the corresponding signals. All the carbon atoms of the aromatic ring are nonequivalent, and, in contrast to compounds **9**−**11**, for which the TCBQ acts as a chelating ligand, only one carbon atom appeared as a doublet (106.9, 117.3, 118.3, 123.9, CCl; 139.9, CO; 155.9, d, J_{PC} = 1.7 Hz, PCO). Single crystals of **12** were grown from an ether solution at −30 °C and subjected to an X-ray diffraction study (Table 2, Figure 3). Derivative **12** is a dipolar $1\sigma^4,2\sigma^3$-diphosphete, in agreement with the spectroscopic data recorded at 183 K. We propose that in solution, at temperatures above 193 K, a dynamic process involving an intramolecular displacement of the coordinated oxygen by the second nucleophilic oxygen atom takes place.

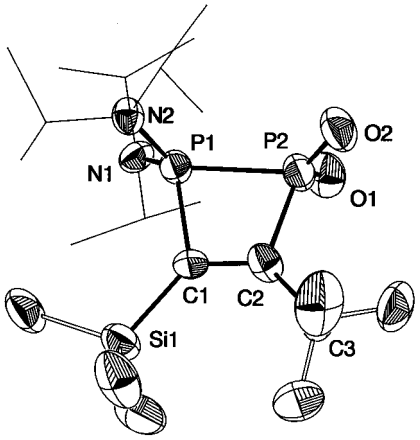


Figure 1. Thermal ellipsoid plot (50% probability) of derivative **7** showing the numbering scheme used. For clarity, hydrogen atoms have been omitted, and isopropyl moieties are shown with the stick model.

Treatment of complex **3** with 1 equiv of tetrabutylammonium fluoride hydrate afforded complex **13**, which was isolated as colorless crystals in 61% yield (Scheme 4). The ring CH was apparent from the ^{1}H NMR spectrum (5.3, dd, J_{PH} = 13.7 and 5.3 Hz); the other NMR data for derivative **13** were very similar to those for complex **3** (Table 1). The structure of compound **13** has been confirmed by an X-ray diffraction study (Table 2, Figure 4). Addition of TCBQ to heterocyclic complex **13** gave rise to the *cis*-1,2-diphosphino alkene complex **14** (77% yield). Compared to derivative **11**, the phosphorus atom bound to TCBQ appeared at much lower field ($\Delta\delta$ = 150 ppm), and the phosphorus possessing the amino substituents at higher field ($\Delta\delta$ = 41 ppm) (Table 1). The $^2J_{PNCH}$ coupling constant of 9.7 Hz is typical for a diisopropylamino-substituted σ^3-phosphorus atom.[10] Lastly, the signal of the sp^2-hybridized *C*-tBu carbon atom of **14** is considerably shielded ($\Delta\delta$ > 40 ppm) compared to that of heterocycles **1**−**13** and appeared in the classical range for an olefinic carbon. The acyclic structure of **14** has been confirmed by an X-ray diffraction study (Table 2, Figure 5).

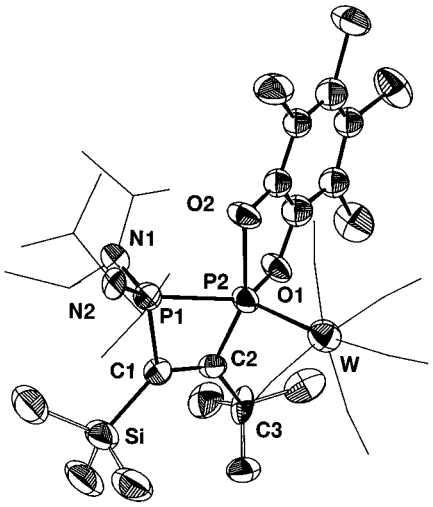
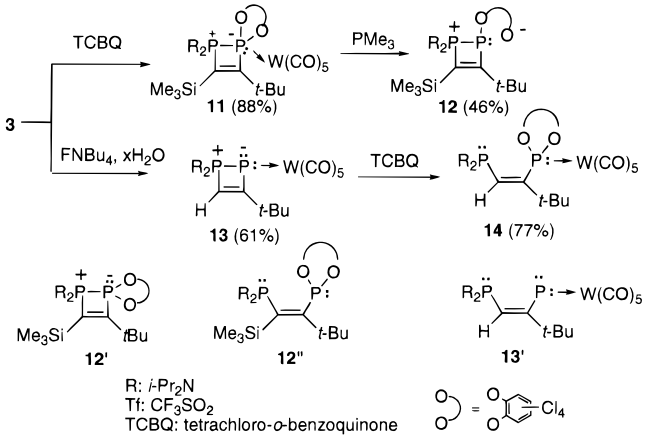


Figure 2. Thermal ellipsoid plot (50% probability) of derivative **11** showing the numbering scheme used. For clarity, hydrogen atoms have been omitted, and isopropyl moieties and carbonyl ligands are shown with the stick model.

Scheme 4



Discussion

In contrast to most diazo derivatives,[3c,d] [bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane does not react as a 1,3-dipole toward *tert*-butylphosphaalkyne. Thus, it can be used as an "*in situ*" precursor of λ^5-phosphaalkyne **15**, which can also be regarded as a phosphinocarbene **15′**.[15] Two mechanisms can account for the formation of $1\sigma^4,2\sigma^2$-diphosphete **1**. Derivative **1** can result from the "head-to-head" codimerization (governed by steric factors) of the λ^3-phosphaalkyne with the λ^5-phosphaalkyne **15**. However, it is known that the carbene **15′** undergoes [1 + 2] cycloaddition reactions with nitriles affording 2-phosphino-*2H*-azirines **16**, which subsequently rearrange in the presence of a suitable catalyst into $1,2\sigma^4$-azaphosphetes **17**.[16] Therefore, it is also possible that the codimerization first produces a transient 2-phosphino-*2H*-phosphirene **18**,[17] which spontaneously undergoes a ring expansion reaction leading to **1** (Scheme 5).

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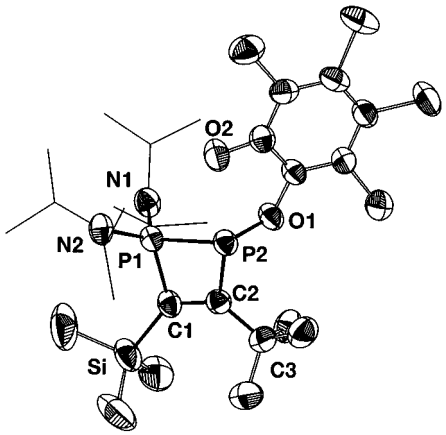

Figure 3. Thermal ellipsoid plot (50% probability) of derivative **12** showing the numbering scheme used. For clarity, hydrogen atoms have been omitted, and isopropyl moieties are shown with the stick model.

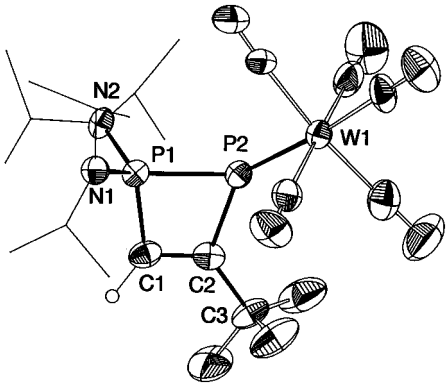

Figure 4. Thermal ellipsoid plot (50% probability) of derivative **13** showing the numbering scheme used. For clarity, hydrogen atoms have been omitted, and isopropyl moieties are shown with the stick model.

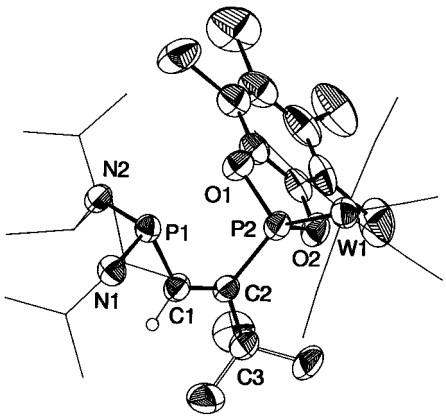

Figure 5. Thermal ellipsoid plot (50% probability) of derivative **14** showing the numbering scheme used. For clarity, hydrogen atoms have been omitted, and isopropyl moieties and carbonyl ligands are shown with the stick model.

Unlike $1\sigma^2,2\sigma^2$-diphosphetes, which are coordinated to transition metals through their π-system,[3] $1\sigma^4,2\sigma^2$-diphosphete **1** acts as an η^1-ligand toward organometallic fragments (Scheme 1). The NMR data for **2** and **3** are very similar to those for the free ligand **1** (Table 1), suggesting that, as already observed for $1,2\sigma^4$-azaphosphetes **17**,[12e] the four-π-electron system is not perturbed when the ring is coordinated to a transition metal fragment. Therefore, the geometric parameters for the coordi-

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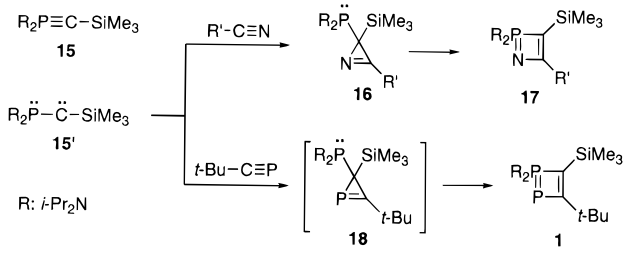
Scheme 5



nated ring (Table 2) are relevant in understanding the electronic structure of the free heterocycle. The ring is planar (mean deviation 0.0278 Å), and the coordinated phosphorus atom is strongly pyramidalized [sum of the angles at P(2): 330.8°]. The value of the phosphorus−phosphorus bond length [2.176(3)Å] is comparable to that observed in free or coordinated phosphanylidene-σ^4-phosphoranes.[6] The endocyclic CC [1.391(10)] and both PC [1.804(7) and 1.842(7)] bond lengths are in the range expected for CC double bonds and PC single bonds, respectively. These geometric parameters as a whole suggest that the heterocycles **1**−**3** feature a localized CC double bond and a strongly polarized PP ylide bond.

The synthesis of compounds **2**−**5** shows that one of the lone pairs of the σ^2-phosphorus atom of **1** is active. More interestingly, the formation of heterocycles **6**−**11** demonstrates that both lone pairs are reactive, which is very rare with linear phosphanylidene-σ^4-phosphoranes.[6g] The σ^2-phosphorus atom of **1** can extend its coordination number up to six without destruction of the four-membered ring skeleton. This is not surprising for compounds **1**−**8** since ring opening through breaking of the P−P bond would generate a stable bis(amino)-phosphine on one side but an unstable low-coordinate phosphorus moiety on the other (a free or coordinated phosphinidene,[18,19] a phosphenium ion,[18,20] a selenexophosphane,[18,21] a diselenexophosphorane,[18,21,22] a dioxophosphorane,[18,23] and a coordinated oxophosphane,[18,24] respectively). Interestingly, derivative **7** can be regarded as a donor-stabilized dioxophosphorane (metaphosphate),[23a,25] a class of compound which has never been characterized by an X-ray diffraction study. This view is supported by the strongly distorted tetrahedron with the PO_2C moiety forming a relatively flat trigonal pyramid (sum of the angles = 353.5°), the large OPO angle [121.2(2)°], and the relatively short PO bond lengths [1.487(4) and 1.483(4) Å]. For compounds **9**−**11**, one might expect that ring cleavage should occur since, on both sides, a stable phosphorus entity would be generated: a bis(amino)phosphine and a phosphonium ion, a phosphorane, and a coordinated phosphine, respectively. Although a few examples of P−P interactions between phosphines and phosphonium ions,[26] or even phosphoranes[26b,27] are known, derivative **11** is certainly the first compound featuring an interaction between a free and a coordinated phosphine.[20b] The value of all the bond lengths compare well with those observed for the other four-membered heterocycles (Table 2), except the P(2)O(2) bond [2.017(6) Å] which is one of the longest PO bonds known so far. However, the geometry around P(2) could not be understood in the absence of the P(2)O(2) bond, since P(2), W, P(1), and O(1) lie in the same plane (maximum deviation from the best plane: 0.048 Å). The molecular geometry about P(2) can be regarded as a distorted trigonal bipyramid,[28] although the value of the C(2)P(2)O(2) angle [153.1(3)°] is small. The excessive steric hindrance around P(2) probably explains both this small value and the nonplanarity of the four-membered ring in **11**.

The persistence of the PP bond in **11** emphasizes that the four-membered ring framework of compounds **1**−**11** is strongly reluctant to undergo ring opening. Therefore the question arises whether a PP interaction between two free phosphines[29] in such a ring could occur. Removing the organometallic fragment from **11** should give the answer. The NMR data for compound **12** show a dynamic process in which the desired compound **12′** is certainly the structure of the transition state. Very surprisingly, the expected $1\sigma^3,2\sigma^3$-*cis*-diphosphinoalkene **12″** is not formed. Instead of breaking the PP bond of the four-membered ring, there is a cleavage of the PO bond of the five-membered ring leading to **12**. The solid state structure (Figure 5) shows that there is no interaction between O(2) and P(2) [O(2)···P(2): 2.328(2) Å] and that the value of the P(1)−P(2) bond length [2.2098(7) Å] is comparable to those observed in the other four-membered heterocycles (Table 2).

From Table 2, it appears that the geometric parameters of the four-membered skeleton are remarkably similar whatever the coordination state of the P(2) atom. Therefore, it becomes clear that the substitution pattern of the endocyclic ethylenic fragment could have a dramatic influence on the persistence of the four-membered ring. Replacement of the silyl group of **3** by a hydrogen atom does not induce a ring opening and has almost no effect on the geometric parameters of the ring (Table 2, Figure 5). This result is not surprising since a ring opening would generate the compound **13′** possessing a highly unstable coordinated phosphinidene.[19] Finally, addition of TCBQ resulted in the ring opening, which led to the formation of the $1\sigma^3,2\sigma^3$-*cis*-diphosphinoalkene complex **14**. The geometric data (Table 2) are very typical for an alkene, the P(1)C(1)C(2) and C(1)C(2)(P2) angles are considerably larger than in the corresponding four-membered heterocycle **11**, and the PP distance (3.389 Å) demonstrates the absence of any PP interaction.

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Conclusions

The unsaturated four-membered ring skeleton is a remarkable template for inducing unusual P−P interactions. Comparing the derivatives **11** and **14**, it is clear that the presence of two very bulky substituents on the ethylenic moiety is the key factor in explaining the persistence of the cyclic structure,[30] especially when the two phosphorus atoms feature a high coordination state, such as in **9**, **10**, and **11**. The formation of **12** instead of **12′** raises the question of a possible PP interaction in $1\sigma^3,2\sigma^3$-*cis*-diphosphinoalkene substituted by bulky groups at both carbon atoms and poor leaving groups at both phosphorus atoms. The nonplanarity of the ring in **11** (Figure 2) is a strong indication that in this case a twisting of the CC double bond[31] would occur allowing the system to escape from the repulsive PP interaction.

Experimental Section

All experiments were performed under an atmosphere of dry argon. Melting points are uncorrected. ^{1}H, ^{13}C, ^{77}Se, and ^{31}P NMR spectra were recorded on Brucker AC80, AC200, WM250, or AMX400 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{77}Se and ^{31}P NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external Me_2Se and 85% H_3PO_4, respectively. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer 1725 X. Mass spectra were obtained on a Ribermag R10 10E instrument. Conventional glassware was used.

$1\sigma^4,2\sigma^2$-Diphosphete 1. An ether solution (30 mL) of [bis-(diisopropylamino)phosphino](trimethylsilyl)diazomethane (1.09 g, 3.15 mmol) and *tert*-butylphosphaalkyne (0.35 g, 3.47 mmol) was irradiated at 254 nm for 5 h at room temperature. After evaporation of the solvent *in vacuo*, $1\sigma^4,2\sigma^2$-diphosphete **1** was obtained as a pale yellow oil (1.18 g, 90% yield): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.28 (s, 9 H, CH_3Si), 1.24 (d, J_{HH} = 6.9 Hz, 12 H, C*H*$_3$CHN), 1.34 (s, 9 H, CH_3C), 1.41 (d, J_{HH} = 6.9 Hz, 12 H, C*H*$_3$CHN), 3.79 (m, 4 H, CH_3CHN); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 4.26 (d, J_{PC} = 2.8 Hz, CH_3Si), 24.66 (d, J_{PC} = 2.4 Hz, *C*H$_3$CHN), 24.71 (d, J_{PC} = 2.4 Hz, *C*H$_3$CHN), 31.10 (d, J_{PC} = 9.8 Hz, *C*H$_3$C), 41.46 (dd, J_{PC} = 17.6 and 52.4 Hz, CH_3C), 48.90 (d, J_{PC} = 5.6 Hz, CH_3CHN), 105.72 (dd, J_{PC} = 36.8 and 4.2 Hz, PCSi), 224.31 (dd, J_{PC} = 54.9 and 9.9 Hz, P*C*t-Bu); ^{31}P NMR ($CDCl_3$, 81.015 MHz) δ +49.17 (dq, J_{PP} = 201.2 Hz, J_{PH} = 13.6 Hz, σ^4-P), +58.43 (d, J_{PP} = 201.2 Hz, σ^2-P); CIMS *m/e* 417 ($M^+ + 1$). Anal. Calcd for $C_{21}H_{46}N_2P_2Si$: C, 60.53; H, 11.13; N, 6.72. Found: C, 60.98; H;,-11.28; N, 6.58.

(η^1-Diphosphete)tetracarbonyliron Complex 2. An ether solution (3 mL) of **1** (1.33 g, 3.19 mmol) was added dropwise, at −78 °C, to an ether solution (5 mL) of iron nonacarbonyl (1.16 g, 3.19 mmol). The solution was allowed to warm to room temperature and stirred overnight, and the solvent and iron pentacarbonyl were removed *in vacuo*. Compound **2** crystallized at −78 °C from a pentane solution as pale-yellow crystals (0.90 g, 48% yield): mp 143−145 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.49 (s, 9 H, CH_3Si), 1.34 (s, 9 H, CH_3C), 1.44 (d, J_{HH} = 6.9 Hz, 24 H, C*H*$_3$CHN), 4.00 (sept d, J_{PH} = 13.4 Hz, J_{HH} = 6.9 Hz, 4 H, CH_3CHN); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 3.55 (d, J_{PC} = 1.0 Hz, CH_3Si), 24.82 (d, J_{PC} = 2.7 Hz, *C*H$_3$CHN), 24.86 (d, J_{PC} = 3.1 Hz, *C*H$_3$CHN), 25.26 (d, J_{PC} = 2.8 Hz, *C*H$_3$CHN), 25.30 (d, J_{PC} = 2.8 Hz, *C*H$_3$CHN), 30.83 (dd, J_{PC} = 4.9 and 2.3 Hz, *C*H$_3$C), 41.65 (dd, J_{PC} = 15.9 and 50.2 Hz, CH_3C), 49.67 (d, J_{PC} = 5.6 Hz, CH_3CHN), 134.72 (dd, J_{PC} = 13.5 and 31.1 Hz, PCSi), 214.03 (dd, J_{PC} = 2.2 and 51.8 Hz, P*C*t-Bu), 216.53 (dd, J_{PC} = 7.8 and 3.8 Hz, CO); ^{31}P NMR ($CDCl_3$, 81.015 MHz) δ +57.41 (dq, J_{PP} = 205.5 Hz, J_{PH} = 13.4 Hz, σ^4-P), +112.65 (d, J_{PP} = 205.5 Hz, PFe); IR (THF) 2023, 1943, 1920 cm^{-1} (CO); EIMS *m/e* 528 (M − 2 CO). Anal. Calcd for $C_{25}H_{46}N_2FeO_4P_2Si$: C, 51.37; H, 7.93; N, 4.79. Found: C, 51.48; H, 8.04; N, 4.87.

(η^1-Diphosphete)pentacarbonyltungsten Complex 3. A THF solution (10 mL) of **1** (1.07 g, 2.57 mmol) was added dropwise at room temperature to a THF solution (50 mL) of $W(CO)_5$(THF) (1.11 g, 2.80 mmol). The solution was allowed to stand for 12 h at room temperature, and the solvent was removed under vacuum. Fractional crystallization at −30 °C from a toluene solution afforded $W(CO)_6$ and derivative **3** as orange crystals (1.43 g, 75% yield): mp 125 °C dec; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.28 (s, 9 H, CH_3Si), 1.32 (s, 9 H, CH_3C), 1.41 (d, J_{HH} = 6.8 Hz, 12 H, C*H*$_3$CHN), 1.49 (d, J_{HH} = 6.8 Hz, 12 H, C*H*$_3$CHN), 3.95 (m, 4 H, CH_3CHN); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 3.27 (d, J_{PC} = 1.0 Hz, CH_3Si), 24.00 (d, J_{PC} = 2.5 Hz, *C*H$_3$CHN), 24.09 (d, J_{PC} = 2.7 Hz, *C*H$_3$CHN), 24.40 (d, J_{PC} = 2.2 Hz, *C*H$_3$CHN), 24.48 (d, J_{PC} = 2.4 Hz, *C*H$_3$CHN), 30.23 (d, J_{PC} = 6.2 Hz, *C*H$_3$C), 41.04 (dd, J_{PC} = 15.8 and 49.2 Hz, CH_3C), 49.10 (d, J_{PC} = 5.2 Hz, CH_3CHN), 126.11 (dd, J_{PC} = 14.2 and 34.9 Hz, PCSi), 198.93 (dd, J_{PC} = 3.4 and 3.4 Hz, J_{WC} = 122.0 Hz, CO_e), 202.41 (d, J_{PC} = 17.3 Hz, CO_a), 209.67 (dd, J_{PC} = 7.1 and 39.2 Hz, P*C*t-Bu); ^{31}P NMR ($CDCl_3$, 81.015 MHz) δ +41.71 (d, J_{PP} = 175.4 Hz, J_{WP} = 115.3 Hz, PW), +57.37 (dq, J_{PP} = 175.4 Hz, J_{PH} = 13.4 Hz, σ^4-P); IR (CH_2Cl_2) 1975, 1930 cm^{-1} (CO); CIMS *m/e* 741 ($M^+ + 1$). Anal. Calcd for $C_{26}H_{46}N_2O_5P_2SiW$: C, 42.17; H, 6.26; N, 3.78. Found: C, 42.29; H, 6.36; N, 3.67.

Cationic $1\sigma^4,2\sigma^3$-Diphosphete 4. Neat methyl trifluoromethanesulfonate (0.062 mL, 0.54 mmol) was added dropwise, at −78 °C, to an ether solution (1 mL) of **1** (0.227 g, 0.54 mmol). The solution was allowed to warm to room temperature and filtered, and the solvent was removed under vacuum. **4** was obtained as a very viscous orange oil (0.30 g, 95% yield): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.30 (s, 9 H, CH_3Si), 1.25 (s, 9 H, CH_3C), 1.34 (d, J_{HH} = 6.9 Hz, 12 H, C*H*$_3$CHN), 1.39 (d, J_{HH} = 6.9 Hz, 12 H, C*H*$_3$CHN), 1.84 (dd, J_{PH} = 4.9 and 19.1 Hz, 3 H, CH_3P), 3.70 (m, 4 H, CH_3CHN); ^{13}C NMR ($CDCl_3$, 62.896 MHz) δ 2.40 (d, J_{PC} = 3.0 Hz, CH_3Si), 11.26 (dd, J_{PC} = 42.0 and 8.5 Hz, PCH_3), 24.34 (d, J_{PC} = 3.2 Hz, *C*H$_3$CHN), 24.75 (d, J_{PC} = 3.9 Hz, *C*H$_3$CHN), 30.36 (dd, J_{PC} = 5.9 and 1.8 Hz, *C*H$_3$C), 40.94 (dd, J_{PC} = 15.7 and 44.0 Hz, CH_3C), 46.92 (d, J_{PC} = 5.2 Hz, CH_3CHN), 50.66 (d, J_{PC} = 4.8 Hz, CH_3CHN), 120.26 (qua, J_{FC} = 320.3 Hz, CF_3), 151.69 (dd, J_{PC} = 9.5 and 36.6 Hz, PCSi), 193.73 (d, J_{PC} = 23.0 Hz, P*C*t-Bu); ^{31}P NMR ($CDCl_3$, 81.015 MHz) δ +40.20 (m, J_{PP} = 107.4 Hz, J_{PH} = 19.1 and 10.9 Hz, σ^4-P), +54.86 (dqua, J_{PP} = 107.4 Hz, J_{PH} = 4.9 Hz, PCH_3). Anal. Calcd for $C_{23}H_{49}N_2F_3O_3P_2SSi$: C, 47.56; H, 8.50; N, 4.82. Found: C, 47.39; H, 8.37; N, 4.65.

$1\sigma^4,2\sigma^3$-Diphosphete 5. A THF solution (1 mL) of **1** (0.555 g, 1.33 mmol) was added dropwise, at room temperature, to a suspension of elemental selenium (0.105 g, 1.33 mmol) in THF (1 mL). After sonication of the solution for 10 min at room temperature, the solvent was removed under vacuum, and the residue was extracted with pentane (10 mL). **5** was obtained as a very air- and moisture-sensitive orange oil which decomposed in solution (0.44 g, 66% yield): ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 2.70 (s, CH_3Si), 25.89 (d, J_{PC} = 2.9 Hz, *C*H$_3$CHN), 26.79 (d, J_{PC} = 5.3 Hz, *C*H$_3$CHN), 30.58 (dd, J_{PC} = 5.7 and 2.7 Hz, *C*H$_3$C), 41.21 (dd, J_{PC} = 16.2 and 48.9 Hz, CH_3C), 47.58 (d, J_{PC} = 2.7 Hz, CH_3CHN), 50.23 (d, J_{PC} = 4.0 Hz, CH_3CHN), 158.50 (dd, J_{PC} = 12.5 and 28.5 Hz, PCSi), 202.44 (dd, J_{PC} = 15.3 and 51.8 Hz, P*C*t-Bu); ^{31}P NMR ($CDCl_3$, 81.015 MHz) δ +39.17 (m, J_{PP} = 246.4 Hz, J_{PH} = 10.5 and 7.8 Hz, σ^4-P), +117.07 (d, J_{PP} = 246.4 Hz, J_{PSe} = 487.4 Hz, PSe); ^{77}Se NMR ($CDCl_3$, 76.323 MHz) δ −63.00 (d, J_{PSe} = 487.4 Hz).

$1\sigma^4,2\sigma^4$-Diphosphete 6. A THF solution (1 mL) of **1** (0.183 g, 0.44 mmol) was added dropwise, at room temperature, to a suspension of elemental selenium (0.104 g, 1.32 mmol) in THF (1 mL). After sonication of the solution for 1 h at room temperature, the solvent was removed under vacuum, and the residue was extracted with pentane (3 × 5 mL). **6** was obtained as a very air- and moisture-sensitive pale yellow oil which decomposed slowly in solution (0.11 g, 43% yield): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.39 (s, 9 H, CH_3Si), 1.37 (d, J_{HH} = 6.9 Hz, 12 H, C*H*$_3$CHN), 1.46 (d, J_{HH} = 6.8 Hz, 12 H, C*H*$_3$CHN), 1.57 (s, 9 H, CH_3C), 4.13 (sept d, J_{PH} = 10.0 Hz, J_{HH} = 6.8 Hz, 4 H, CH_3CHN); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 3.66 (s, CH_3Si), 24.53

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(d, J_{PC} = 3.5 Hz, *C*H_3CHN), 25.19 (d, J_{PC} = 2.8 Hz, *C*H_3CHN), 31.50 (dd, J_{PC} = 4.0 and 1.7 Hz, *C*H_3C), 41.84 (dd, J_{PC} = 13.7 and 47.8 Hz, CH_3*C*), 49.79 (d, J_{PC} = 3.0 Hz, CH_3*C*HN), 135.46 (dd, J_{PC} = 18.3 and 25.6 Hz, PCSi), 194.89 (dd, J_{PC} = 22.6 and 53.3 Hz, P*C*t-Bu); ^{31}P NMR ($CDCl_3$, 81.015 MHz) δ +59.19 (dq, J_{PP} = 47.1 Hz, J_{PH} = 10.0 Hz, σ^4-P), +83.22 (d, J_{PP} = 47.1 Hz, J_{PSe} = 698.9 Hz, PSe_2); ^{77}Se NMR ($CDCl_3$, 76.323 MHz) δ +264.78 (d, J_{PSe} = 698.9 Hz); CIMS *m/e* 577 ($M^+ + 1$). Anal. Calcd for $C_{21}H_{46}N_2P_2Se_2S$: C, 43.90; H, 8.07; N, 4.88. Found: C, 43.69; H, 7.82; N, 4.68.

$1\sigma^4,2\sigma^4$-Diphosphete 7. A CH_2Cl_2 solution (1 mL) of bis(trimethylsilyl)peroxide (0.41 g, 2.28 mmol) was added dropwise, at −78 °C, to a CH_2Cl_2 solution (1 mL) of **1** (0.32 g, 0.76 mmol). The solution was allowed to warm to room temperature, the solvent was removed under vacuum, and the residue was extracted with pentane (3 × 5 mL). **7** was isolated by crystallization from a CH_2Cl_2/pentane solution at −30 °C as colorless crystals (0.29 g, 84% yield): mp 95−97 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.41 (s, 9 H, CH_3Si), 1.40 (d, J_{HH} = 6.8 Hz, 12 H, C*H*$_3$CHN), 1.43 (d, J_{HH} = 6.8 Hz, 12 H, C*H*$_3$CHN), 1.43 (s, 9 H, CH_3C), 3.79 (sept d, J_{PH} = 13.3 Hz, J_{HH} = 6.8 Hz, 4 H, CH_3C*H*N); ^{13}C NMR ($CDCl_3$, 100.630 MHz) δ 3.22 (s, CH_3Si), 23.95 (s, *C*H_3CHN), 24.16 (s, *C*H_3CHN), 30.51 (d, J_{PC} = 4.2 Hz, *C*H_3C), 39.51 (dd, J_{PC} = 12.9 and 50.0 Hz, CH_3*C*), 49.16 (d, J_{PC} = 4.2 Hz, CH_3*C*HN), 141.04 (dd, J_{PC} = 20.4 and 28.3 Hz, PCSi), 199.90 (dd, J_{PC} = 78.7 and 105.3 Hz, P*C*t-Bu); ^{31}P NMR ($CDCl_3$, 32.438 MHz) δ +44.52 (d, J_{PP} = 6.7 Hz, PO_2), +114.11 (qd, J_{PH} = 13.3 Hz, J_{PP} = 6.7 Hz, σ^4-P). Anal. Calcd for $C_{21}H_{46}N_2O_2P_2Si$: C, 56.22; H, 10.33; N, 6.24. Found: C, 56.39; H, 10.47; N, 6.39.

(η^1-Diphosphete)pentacarbonyltungsten Complex 8. A CH_2Cl_2 solution (1 mL) of bis(trimethylsilyl)peroxide (0.08 g, 0.43 mmol) was added dropwise at −78 °C to a CH_2Cl_2 solution (1 mL) of **3** (0.32 g, 0.43 mmol). The solution was allowed to warm to room temperature, the solvent was removed under vacuum, and the residue was extracted with pentane (3 × 5 mL). Complex **8** was isolated as a yellow oil (0.22 g, 68% yield): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.41 (s, 9 H, CH_3Si), 1.48 (s, 9 H, CH_3C), 1.51 (d, J_{HH} = 6.9 Hz, 12 H, C*H*$_3$CHN), 1.55 (d, J_{HH} = 6.9 Hz, 12 H, C*H*$_3$CHN), 3.71 (sept d, J_{PH} = 10.9 Hz, J_{HH} = 6.9 Hz, 2 H, CH_3C*H*N), 4.07 (sept d, J_{PH} = 10.9 Hz, J_{HH} = 6.9 Hz, 2 H, CH_3C*H*N); ^{13}C NMR ($CDCl_3$, 100.630 MHz) δ 3.54 (s, CH_3Si), 24.08 (d, J_{PC} = 4.2 Hz, *C*H_3CHN), 24.37 (d, J_{PC} = 4.0 Hz, *C*H_3CHN), 25.24 (d, J_{PC} = 2.7 Hz, *C*H_3CHN), 26.19 (s, *C*H_3CHN), 31.33 (dd, J_{PC} = 2.8 and 2.7 Hz, *C*H_3C), 40.67 (dd, J_{PC} = 15.0 and 52.1 Hz, CH_3*C*), 48.63 (d, J_{PC} = 6.4 Hz, CH_3*C*HN), 51.93 (d, J_{PC} = 3.9 Hz, CH_3*C*HN), 144.62 (dd, J_{PC} = 7.4 and 13.1 Hz, PCSi), 198.40 (dd, J_{PC} = 7.3 and 1.1 Hz, J_{WC} = 127.1 Hz, CO_e), 201.15 (d, J_{PC} = 24.9 Hz, CO_a), 201.38 (dd, J_{PC} = 1.8 and 48.0 Hz, P*C*t-Bu); ^{31}P NMR ($CDCl_3$, 162.000 MHz) δ +72.44 (dq, J_{PP} = 110.9 Hz, J_{PH} = 10.9 Hz, σ^4-P), +160.80 (d, J_{PP} = 110.9 Hz, J_{WP} = 265.0 Hz, PW). Anal. Calcd for $C_{26}H_{46}N_2O_6P_2SiW$: C, 41.27; H, 6.13; N, 3.70. Found: C, 41.01; H, 6.00; N, 3.55.

Cationic $1\sigma^4,2\sigma^5$-Diphosphete 9. An ether solution (1 mL) of TCBQ (0.15 g, 0.61 mmol) was added dropwise, at −78 °C, to an ether solution (1 mL) of **4** (0.35 g, 0.61 mmol). The mixture was allowed to warm to room temperature and filtered, and the solvent was removed under vacuum. **9** was isolated as an orange oil (0.43 g, 86% yield): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.50 (s, 9 H, CH_3Si), 1.24 (d, J_{HH} = 6.8 Hz, 6 H, C*H*$_3$CHN), 1.27 (d, J_{HH} = 6.8 Hz, 6 H, C*H*$_3$CHN), 1.29 (d, J_{HH} = 6.8 Hz, 6 H, C*H*$_3$CHN), 1.32 (d, J_{HH} = 6.8 Hz, 6 H, C*H*$_3$CHN), 1.55 (s, 9 H, CH_3C), 2.30 (dd, J_{PH} = 8.6 and 7.6 Hz, 3 H, PCH_3), 3.73 (sept d, J_{PH} = 10.0 Hz, J_{HH} = 6.8 Hz, 2 H, CH_3C*H*N), 3.91 (sept d, J_{PH} = 13.6 Hz, J_{HH} = 6.8 Hz, 2 H, CH_3C*H*N); ^{13}C NMR ($CDCl_3$, 100.630 MHz) δ 2.92 (dd, J_{PC} = 2.1 and 1.9 Hz, CH_3Si), 20.94 (dd, J_{PC} = 66.1 and 4.0 Hz, PCH_3), 24.52 (m, *C*H_3CHN), 25.02 (dd, J_{PC} = 3.6 and 2.1 Hz, *C*H_3CHN), 25.93 (dd, J_{PC} = 2.1 and 1.9 Hz, *C*H_3CHN), 31.33 (dd, J_{PC} = 2.1 and 1.5 Hz, *C*H_3C), 41.53 (dd, J_{PC} = 9.3 and 51.9 Hz, CH_3*C*), 50.14 (dd, J_{PC} = 8.0 and 1.9 Hz, CH_3*C*HN), 52.64 (d, J_{PC} = 3.6 Hz, CH_3*C*HN), 115.24 (dd, J_{PC} = 6.6 and 4.2 Hz, OC*C*), 116.54 (d, J_{PC} = 12.3 Hz, OC*C*), 120.20 (qua, J_{FC} = 319.6 Hz, CF_3), 124.29 (s, OCC*C*), 127.36 (s, OCC*C*), 138.28 (d, J_{PC} = 2.5 Hz, OC), 142.17 (dd, J_{PC} = 26.5 and 44.2 Hz, PCSi), 144.24 (dd, J_{PC} = 4.0 and 8.5 Hz, OC), 209.92 (dd, J_{PC} = 7.6 and 85.0 Hz, P*C*t-Bu); ^{31}P NMR ($CDCl_3$, 81.015 MHz) δ +25.24 (dqua, J_{PP} = 35.8 Hz, J_{PH} = 8.6 Hz, σ^5-P), +117.00 (m, J_{PP} = 35.8 Hz, σ^4-P). Anal. Calcd for $C_{29}H_{49}N_2Cl_4F_3O_5P_2SSi$: C, 42.13; H, 5.97; N, 3.39. Found: C, 42.40; H, 6.14; N, 3.20.

$1\sigma^4,2\sigma^6$-Diphosphete 10. An ether solution (1 mL) of TCBQ (0.34 g, 1.40 mmol) was added dropwise, at −78 °C, to an ether solution (2 mL) of **1** (0.29 g, 0.70 mmol). The solution was allowed to warm to room temperature, the solvent was removed under vacuum, and the residue was extracted with pentane (3 × 5 mL). **10** was isolated by crystallization from a CH_2Cl_2 solution at −30 °C as colorless crystals (0.59 g, 92% yield): mp 223−224 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.46 (s, 9 H, CH_3Si), 1.16 (d, J_{HH} = 8.5 Hz, 6 H, C*H*$_3$CHN), 1.20 (d, J_{HH} = 8.6 Hz, 6 H, C*H*$_3$CHN), 1.26 (s, 9 H, CH_3C), 1.50 (d, J_{HH} = 6.3 Hz, 6 H, C*H*$_3$CHN), 1.53 (d, J_{HH} = 6.4 Hz, 6 H, C*H*$_3$CHN), 3.84 (sept d, J_{PH} = 9.0 Hz, J_{HH} = 6.9 Hz, 2 H, CH_3C*H*N), 4.24 (sept d, J_{PH} = 9.0 Hz, J_{HH} = 6.9 Hz, 2 H, CH_3C*H*N); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 5.09 (dd, J_{PC} = 1.7 and 2.1 Hz, CH_3Si), 23.84 (dd, J_{PC} = 3.4 and 1.9 Hz, *C*H_3CHN), 25.24 (dd, J_{PC} = 3.6 and 1.3 Hz, *C*H_3CHN), 25.37 (dd, J_{PC} = 3.4 and 2.1 Hz, *C*H_3CHN), 25.60 (dd, J_{PC} = 2.1 and 1.3 Hz, *C*H_3CHN), 31.29 (dd, J_{PC} = 3.8 and 1.4 Hz, *C*H_3C), 40.10 (dd, J_{PC} = 15.4 and 55.1 Hz, CH_3*C*), 49.31 (dd, J_{PC} = 4.5 and 1.8 Hz, CH_3*C*HN), 50.86 (d, J_{PC} = 4.3 Hz, CH_3*C*HN), 113.32 (d, J_{PC} = 8.6 Hz, OC*C*), 113.64 (dd, J_{PC} = 13.5 and 5.3 Hz, OC*C*), 114.25 (d, J_{PC} = 14.1 Hz, OC*C*), 114.49 (dd, J_{PC} = 9.1 and 1.9 Hz, OC*C*), 121.73, 122.25, 122.52, 122.57 (s, OCC*C*), 130.50 (dd, J_{PC} = 13.9 and 39.2 Hz, PCSi), 142.77 (dd, J_{PC} = 4.3 and 4.7 Hz, OC), 142.80 (d, J_{PC} = 1.0 Hz, OC), 143.02 (d, J_{PC} = 4.2 Hz, OC), 144.99 (d, J_{PC} = 3.4 Hz, OC), 207.04 (dd, J_{PC} = 89.1 and 120.4 Hz, P*C*t-Bu); ^{31}P NMR ($CDCl_3$, 81.015 MHz) δ −65.45 (d, J_{PP} = 122.1 Hz, PO_4), +131.28 (dq, J_{PP} = 122.1 Hz, J_{PH} = 9.0 Hz, σ^4-P). Anal. Calcd for $C_{33}H_{46}N_2Cl_8O_4P_2Si$: C, 43.63; H, 5.10; N, 3.08. Found: C, 43.72; H, 5.24; N, 3.00.

(η^1-Diphosphete)pentacarbonyltungsten Complex 11. A THF solution (2 mL) of TCBQ (0.80 g, 0.41 mmol) was added dropwise, at −78 °C, to a THF solution (1 mL) of **3** (0.30 g, 0.41 mmol). The solution was allowed to warm to room temperature and filtered, and the solvent was removed under vacuum. The residue was extracted with ether (3 × 5 mL), and **11** was isolated by crystallization from a CH_2Cl_2 solution at −30 °C as pale yellow crystals (0.36 g, 88% yield): mp 91 °C dec; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.45 (s, 9 H, CH_3Si), 1.20−1.35 (m, 24 H, C*H*$_3$CHN), 1.31 (s, 9 H, CH_3C), 3.50−4.00 (m, 4 H, CH_3C*H*N); ^{13}C NMR ($CDCl_3$, 100.630 MHz) δ 3.44 (s, CH_3Si), 24.86 (d, J_{PC} = 4.5 Hz, *C*H_3CHN), 24.95 (dd, J_{PC} = 2.2 and 2.3 Hz, *C*H_3CHN), 25.68 (d, J_{PC} = 3.2 Hz, *C*H_3CHN), 26.91 (s, *C*H_3CHN), 31.93 (d, J_{PC} = 2.1 Hz, *C*H_3C), 40.73 (dd, J_{PC} = 10.6 and 55.1 Hz, CH_3*C*), 49.80 (dd, J_{PC} = 8.7 and 2.1 Hz, CH_3*C*HN), 52.37 (s, CH_3*C*HN), 114.58 (dd, J_{PC} = 6.4 and 1.8 Hz, OC*C*), 115.87 (d, J_{PC} = 8.6 Hz, OC*C*), 124.78 (s, OCC*C*), 125.25 (s, OCC*C*), 130.00 (dd, J_{PC} = 27.0 and 40.4 Hz, PCSi), 140.86 (dd, J_{PC} = 2.1 and 2.1 Hz, OC), 149.77 (d, J_{PC} = 6.8 Hz, OC), 198.31 (d, J_{PC} = 8.1 Hz, J_{WC} = 127.5 Hz, CO_e), 199.62 (d, J_{PC} = 34.5 Hz, CO_a), 215.43 (dd, J_{PC} = 41.9 and 73.6 Hz, P*C*t-Bu); ^{31}P NMR ($CDCl_3$, 161.986 MHz) δ +74.32 (J_{PP} = 25.1 Hz, J_{WP} = 299.3 Hz, PW), +80.42 (dq, J_{PP} = 25.1 Hz, J_{PH} = 12.3 Hz, σ^4-P). Anal. Calcd for $C_{32}H_{46}N_2Cl_4O_7P_2SiW$: C, 38.96; H 4.70; N, 2.84. Found: C, 39.09; H, 4.78; N, 2.89.

Zwitterionic $1\sigma^4,2\sigma^3$-Diphosphete 12. A toluene solution (0.4 mL) of trimethylphosphine (0.40 mmol) was added dropwise, at −78 °C, to a THF solution (1 mL) of **11** (0.20 g, 0.20 mmol). The solution was allowed to warm to room temperature and stirred for 12 h at room temperature. The solvent and excess trimethylphosphine were removed under vacuum, and the residue was extracted with pentane (3 × 5 mL). **12** was isolated by crystallization from an ether solution at −30 °C as pale yellow crystals (0.05 g, 46% yield): mp 121−123 °C dec; ^{1}H NMR ($CDCl_3$, 400 MHz, 293 K) δ 0.42 (s, 9 H, CH_3Si), 1.31 (d, J_{HH} = 6.9 Hz, 6 H, C*H*$_3$CHN), 1.39 (d, J_{HH} = 6.9 Hz, 6 H, C*H*$_3$CHN), 1.44 (d, J_{HH} = 6.9 Hz, 6 H, C*H*$_3$CHN), 1.44 (s, 9 H, CH_3C), 1.51 (d, J_{HH} = 6.9 Hz, 6 H, C*H*$_3$CHN), 3.98 (sept d, J_{PH} = 10.0 Hz, J_{HH} = 6.9 Hz, 4 H, CH_3C*H*N); ^{13}C NMR ($CDCl_3$, 100.630 MHz, 293K) δ 1.64 (s, CH_3Si), 23.45 (d, J_{PC} = 2.6 Hz, *C*H_3CHN), 23.51 (d, J_{PC} = 2.6 Hz, *C*H_3CHN), 23.75 (dd, J_{PC} = 2.4 Hz, *C*H_3CHN), 23.77 (d, J_{PC} = 2.4 Hz, *C*H_3CHN), 24.44 (d, J_{PC} = 2.8 Hz, *C*H_3CHN), 25.14 (d, J_{PC} = 3.9 Hz, *C*H_3CHN), 29.67 (dd, J_{PC} = 4.3 and 1.4 Hz, *C*H_3C), 39.43 (dd, J_{PC} = 13.7 and 47.9 Hz, CH_3*C*), 47.76 (d, J_{PC} = 5.4 Hz, CH_3*C*HN), 47.82 (d, J_{PC} = 5.4 Hz, CH_3*C*HN), 51.83 (d, J_{PC} = 4.3 Hz, CH_3*C*HN), the other carbon atoms are not observed. ^{31}P NMR ($CDCl_3$, 161.990

MHz, 293 K) δ +61.97 (dq, J_{PP} = 213.9 Hz, J_{PH} = 10.0 Hz, σ^4-P), +138.58 (d, J_{PP} = 213.9 Hz, PO). ^{13}C NMR (CD_2Cl_2, 100.630 MHz, 183K) δ 3.01 (s, CH_3Si), 21.12, 21.63, 22.95, 24.11, 24.89, 25.51 (s broad *C*H_3CHN), 29.07 (d, J_{PC} = 2.0 Hz, *C*H_3C), 38.46 (dd, J_{PC} = 14.1 and 45.6 Hz, CH_3*C*), 45.44, 47.93, 50.00, 51.19 (s broad, CH_3*C*HN), 106.92 (s, OC*C*), 117.27 (s, OCC*C*), 118.28 (s, OCC*C*), 123.88 s, OCC*C*), 139.94 (s, OC), 152.06 (dd, J_{PC} = 12.7 and 32.2 Hz, PCSi), 155.93 (d, J_{PC} = 1.7 Hz, OC), 198.36 (dd, J_{PC} = 15.3 and 28.4 Hz, P*C*t-Bu); ^{31}P NMR (CD_2Cl_2, 161.990 MHz, 183K) δ +54.23 (dq, J_{PP} = 200.8 Hz, J_{PH} = 21.9 Hz, σ^4-P), +164.49 (d, J_{PP} = 200.8 Hz, PO). Anal. Calcd for $C_{27}H_{46}N_2Cl_4O_2P_2Si$: C, 48.94; H 7.00; N, 4.23. Found: C, 49.06; H, 7.09; N, 4.31.

(η^1-Diphosphete)pentacarbonyltungsten Complex 13. Neat tetrabutylammonium fluoride hydrate (0.06 g, 0,24 mmol) was added, at −78 °C, to an ether solution (1 mL) of **3** (0.18 g, 0.24 mmol). The solution was allowed to warm to room temperature, the solvent was removed under vacuum, and the residue was extracted with pentane (3 × 5 mL). **13** was isolated by crystallization from an ether solution at −30 °C as colorless crystals (0.10 g, 61% yield): mp 116 °C dec; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.17 (d, J_{PH} = 0.7 Hz, 9 H, CH_3C), 1.30 (d, J_{HH} = 6.8 Hz, 12 H, C*H*$_3$CHN), 1.31 (d, J_{HH} = 6.8 Hz, 12 H, C*H*$_3$-CHN), 3.74 (sept d, J_{HH} = 6.8 Hz, J_{PH} = 16.1 Hz, 4 H, CH_3C*H*N), 5.31 (dd, J_{PH} = 13.7 and 5.3 Hz, 1 H, PCH); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 23.06 (s broad, *C*H_3CHN), 23.30 (s, *C*H_3CHN), 28.70 (dd, J_{PC} = 3.7 and 1.7 Hz, *C*H_3C), 38.33 (dd, J_{PC} = 11.9 and 41.7 Hz, CH_3*C*), 48.24 (d, J_{PC} = 4.5 Hz, CH_3*C*HN), 111.23 (dd, J_{PC} = 17.8 and 72.6 Hz, PCH), 193.66 (dd, J_{PC} = 17.3 and 42.6 Hz, P*C*t-Bu), 199.80 (t-like, J_{PC} = 5.1, J_{wc} = 126.4 Hz, CO_e), 203.28 (d, J_{PC} = 14.5 Hz, CO_a); ^{31}P NMR ($CDCl_3$, 81.015 MHz) δ +45.18 (ddq, J_{PP} = 220.4 Hz, J_{PH} = 13.7 and 16.1 Hz, J_{WP} = 12.0 Hz, σ^4-P), +68.22 (dd, J_{PP} = 220.4 Hz, J_{PH} = 5.3 Hz, J_{WP} = 98.5 Hz, PW); IR (CH_2Cl_2) 1931, 1899 cm^{-1} (CO). Anal. Calcd for $C_{23}H_{38}N_2O_5P_2W$: C, 41.33; H, 5.73; N, 4.19. Found: C, 41.22; H, 5.67; N, 4.14.

Alkenylphosphine Complex 14. A suspension of TCBQ (0.04 g, 0.17 mmol) in pentane (2 mL) was added, at −78 °C, to a suspension of **13** (0.11 g, 0.17 mmol) in pentane (1 mL). The solution was allowed to warm to room temperature and filtered, and the solvent was removed under vacuum. The residue was extracted with pentane (3 × 5 mL), and **13** was isolated by crystallization from an ether solution at −30 °C as colorless crystals (0.12 g, 77% yield): mp 134−136 °C dec; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.18 (d, J_{HH} = 6.4 Hz, 12 H, C*H*$_3$CHN), 1.26 (d, J_{HH} = 6.4 Hz, 12 H, C*H*$_3$CHN), 1.35 (s, 9 H, CH_3C), 3.48 (sept d, J_{PH} = 11.2 Hz, J_{HH} = 6.4 Hz, 4 H, CH_3C*H*N), 7.16 (dd, J_{PH} = 4.6 and 40.7 Hz, 1 H, PCH); ^{13}C NMR ($CDCl_3$, 100.625 MHz) δ 24.62 (d, J_{PC} = 3.3 Hz, *C*H_3CHN), 30.84 (d, J_{PC} = 1.8 Hz, *C*H_3C), 39.04 (dd, J_{PC} = 9.7 and 6.3 Hz, CH_3*C*), 47.26 (d, J_{PC} = 9.7 Hz, CH_3*C*HN), 116.19 (d, J_{PC} = 6.9 Hz, OC*C*), 126.36 (s, OCC*C*), 142.04 (dd, J_{PC} = 8.5 and 20.8 Hz, PCH), 143.42 (d, J_{PC} = 5.8 Hz, OC), 154.22 (d, J_{PC} = 28.7 Hz, PCt-Bu), 194.82 (dd, J_{PC} = 3.8 and 8.3 Hz, J_{WC} = 138.6 Hz, CO_e), 197.76 (d, J_{PC} = 38.1 Hz, CO_a); ^{31}P NMR ($CDCl_3$, 161.990 MHz) δ +38.95 (ddq, J_{PP} = 24.5 Hz, J_{PH} = 4.6 and 11.2 Hz, σ^4-P),+ 224.49 (dd, J_{PP} = 24.5 Hz, J_{PH} = 40.7 Hz, J_{WP} = 350.9 Hz, PW); IR (CH_2Cl_2) 2084, 1969, 1957 cm^{-1} (CO). Anal. Calcd for $C_{29}H_{38}N_2Cl_4O_7P_2W$: C, 38.10; H, 4.19; N, 3.06. Found: C, 38.25; H, 4.19; N, 3.00.

Solution and Refinement of Structures 7 and 11−14. Crystal data for all structures are presented in Table 3. All data were collected at room temperature. The data of the structures **7** and **12**−**14** were collected on a STOE-IPDS diffractometer with MoKα (λ = 0.71073 Å) radiation using φ-scans. The data for **11** were measured on an Enraf-Nonius CAD4 diffractometer with MoKα (λ = 0.71073 Å) radiation using ω-2θ scans. A semiempirical absorption correction was employed for structure **11**. The structures were solved by direct methods using *SHELXS-90*[32] and refined with all data on F^2 with a weighting scheme of $\omega^{-1} = \sigma^2(F_o^2) + (g1 \cdot P)^2 + (g2 \cdot P)$ with $P = (F_o^2 + 2F_c^2)/3$ using *SHELXL-93*.[33] All non-hydrogen atoms were treated anisotropically. For the atom C27 in structure **12** a disorder in two positions was found and refined with an occupancy of 0.5/0.5. All hydrogen atoms were located by difference Fourier maps.

Acknowledgment. We are grateful to the Humboldt Foundation for a grant to H. G. and an award to G.B. and to the CNRS for financial support of this work.

Supporting Information Available: Tables of crystal and intensity collection data, position and thermal parameters, interatomic distances and angles for derivatives **7** and **11**−**14** (39 pages). See any current masthead page for ordering and Internet access instructions.

JA971821F