Multifunctional 2*H*-1,2-Azaphosphole Complexes: A Good Starting Point for the Synthesis of Functional 1,2-Azaphospholide Complexes?

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The thermolysis of *P*-functionalized 7-phosphanorbornadiene tungsten complexes **3a**−**d** in *o*-xylene at 120 °C in the presence of various carbonitriles and dimethyl acetylenedicarboxylate (DMAD) has been investigated. The reaction of complex **3a**, 1-piperidino carbonitrile, and DMAD yielded a product mixture, whereby 2*H*-1,2-azaphosphole complex **6** was formed in ca. 40−45% yield together with diazaphosphole complexes **7** (ca. 10−15%) and **8** (ca. 10−15%) and other nonidentified products (ca. 30%). Unfortunately, none of these products could be separated by column chromatography. In marked contrast, reactions of 7-phosphanorbornadiene tungsten complexes **3a**−**d** with triphenylphosphane-imino carbonitrile and DMAD led to *P*-functionalized 2*H*-1,2-azaphosphole complexes **11a**−**d** in good to excellent yields. Preliminary investigations of decomplexation reactions revealed a remarkable thermal stability of **11a**−**d**: no reaction occurred with bis(diphenylphosphino)ethane (DPPE) at 140 °C. Preliminary studies of exocyclic P−C bond cleavage reactions of 2*H*-1,2-azaphosphole complexes **11a**,**b** using potassium *tert*-butanolate (KO*t*Bu) showed instantaneous reactions and color change from yellow to dark red; an intermediate was detected by ^{31}P NMR spectroscopy. Treatment with an excess of methyl iodide led to one major product, which, most probably, is the *N*-methyl-substituted 1*H*-1,2-azaphosphole complex **13**; unfortunately, chromatography failed and it could only be observed by ^{31}P NMR spectroscopy. A comparative study on P−C bond cleavage/methylation reactions using monofunctional 2*H*-1,3,2-diazaphosphole complex **14** and the system KO*t*Bu/methyl iodide showed the selective formation of the *P*-methyl-substituted 2*H*-1,3,2-diazaphosphole complex **16**; complexes **14** and **16** were prepared using the Cu(I)Cl route. Complexes **11a**−**d**, **14**, and **16** were characterized by elemental analyses, NMR, UV/vis, IR, and mass spectroscopy and, in addition, by single-crystal X-ray diffraction in the case of **11a**−**d**. Additionally, we investigated selected isomers of lithium and potassium 1,2-azaphospholides by ab initio calculations using HF and MP2/6-311++G(2d,p) level of theory; stability, structure, and aromaticity aspects are discussed.

Introduction

In recent years, we have studied the synthesis of 2*H*-1,2-azaphosphole complexes **IV** using three-component reactions of 2*H*-azaphosphirene complexes **I**,[1] nitriles, and alkynes,[2,3] thus forming transient nitrilium phosphane-ylide complexes **III** via 1,1-addition of nitriles and electrophilic terminal phosphanediyl complexes[4] **II** (Scheme 1). The synthetic utility of transient nitrilium phosphane-ylide complexes in organophosphorus chemistry[5] motivated us to extend their chemistry by using

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⊥ Laboratoire Hétéroéléments et Coordination.

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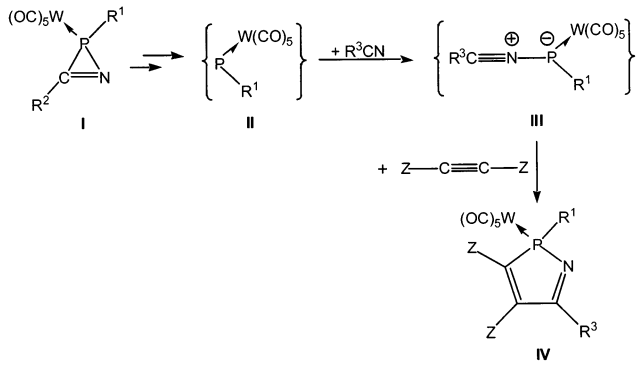
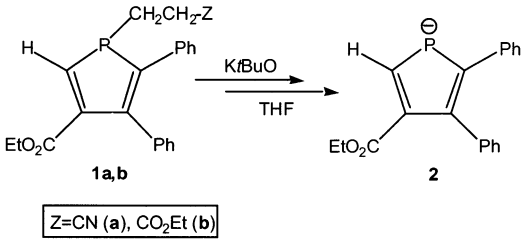
Scheme 1. Synthesis of 2*H*-1,2-Azaphosphole Complexes



7-phosphanorbornadiene complexes and 1-piperidino carbonitrile in the presence[6] or absence[7] of dimethyl acetylenedicarboxylate (DMAD). In these cases, we observed similar reactivity of the nitrilium phosphaneylide complexes thus generated. Nevertheless, there were two remarkable differences, namely, different π-bond selectivity and regioselectivity: both were explained by assuming less sterically crowded transition states of the [3+2] cycloaddition reactions.[6,7]

Although we were now able to synthesize a variety of 2*H*-1,2-azaphosphole complexes, two main targets in this area still remained: The synthesis of noncoordinated 2*H*-1,2-azaphospholes[8] and 1,2-azaphospholides,[9] the latter in a main group- or transition metal-coordinated fashion. In view of the central importance of anionic 6π-aromatic ligand systems such as cyclopentadienides[10] and phospholides[11,12] in coordination and organometallic chemistry, 1,2-azaphospholides could be envisaged as promising novel 6π-aromatic ligands. Therefore, we felt encouraged to use *P*-functional 7-phosphanorbornadiene complexes, which could give rise to 1,2-azaphospholide complexes using mild procedures that were originally developed to access functional phospholides; for example, cleavage of the exocyclic P−C bond of β-ethyl-functionalized phosphole complexes **1a**,**b** was achieved with potassium *tert*-butanolate to furnish phospholide **2** (Scheme 2).[13] This methodology was also successful if the phosphorus is coordinated to a transition metal, e.g., in 1,2-dihydro-1,2-diphosphinine complexes.[14]

Scheme 2. Established Approach to Functional Phospholides



Here, we report the synthesis and structures of multifunctional 2*H*-1,2-azaphosphole complexes and reactions thereof, which provide evidence by phosphorus NMR for the intermediate generation of 1,2-azaphospholide complexes. Furthermore, comparative reactions of a monofunctional 2*H*-1,3,2-diazaphosphole complex provide strong evidence for the formation of a 1,3,2-diazaphospholide derivative and thus further indirect support for our assumption of the 1,2-azaphospholide formation. We also report ab initio calculations of stability, structure, and aromaticity of selected isomers of lithium and potassium 1,2-azaphospholides at the HF and rMP2(fc)/6-311++G(2d,p) level of theory.

Results

We initially focused our attention on the transient generation of nitrilium phosphane-ylide complexes with *P*-functional substituents and their [3+2] trapping with DMAD. Because of our previous success in employing 1-piperidino carbonitrile as carbonitrile component, we first studied the thermal decomposition of 7-phosphanorbornadiene complex **3a**[15] in *o*-xylene at 120 °C in the presence of 2 equiv of carbonitrile **4a** and DMAD (**5**). Although the targeted 2*H*-1,2-azaphosphole complex **6** was probably formed (δ ^{31}P = 79.6, ^{1}J(W,P) = 253.6 Hz) (ca. 40−45%), the outcome was disappointing because of the formation of a complicated product mixture (Scheme 3). Other products such as the regioisomeric diazaphosphole complexes **7**[7] (ca. 10−15%) and **8**[7] (ca. 10−15%) were identified using authentic samples. Other byproducts were formed in small amounts (altogether ca. 30%; δ ^{31}P = 214.4, 205.6, 123.3, 76.4, and 71.2) but could not be identified. Probably, these products stem from competing reactions in which the β-ethyl carbonitrile group is involved. Unfortunately, all attempts to isolate complex **6** (or the other products) by column chromatography failed. Nevertheless, this tentative structural assignment of **6** seems plausible because of the similar ^{31}P NMR data of **6** and those of the previously characterized, closely related *P*-methyl and *P*-phenyl 2*H*-1,2-azaphosphole complexes (δ ^{31}P = 74.8, ^{1}J(W,P) = 249.1 Hz, P-Me and δ ^{31}P = 79.0, ^{1}J(W,P) = 256.3 Hz, P-Ph).[6]

We knew from our recent studies[16] that three-component reactions using 2*H*-azaphosphirene complexes, alkynes, and carbonitriles with strong π-donating substituents such as the triphenylphosphane-imino substituent yield transient nitrilium phosphane-ylide complexes that react more selectively than *C*-dialkyl-

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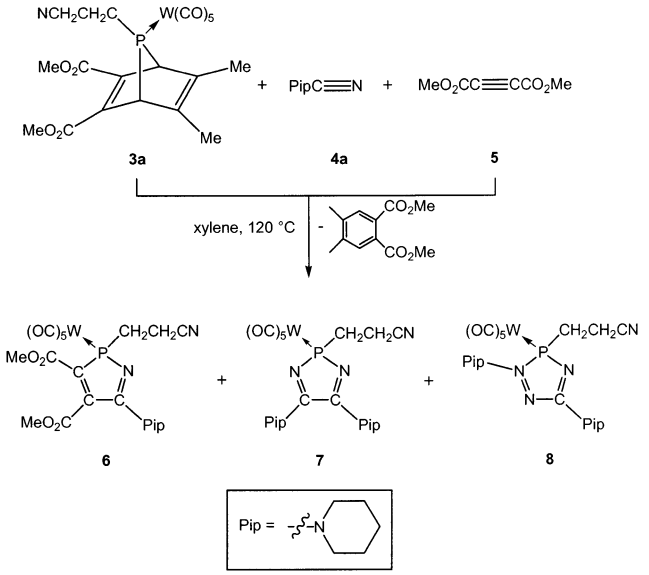
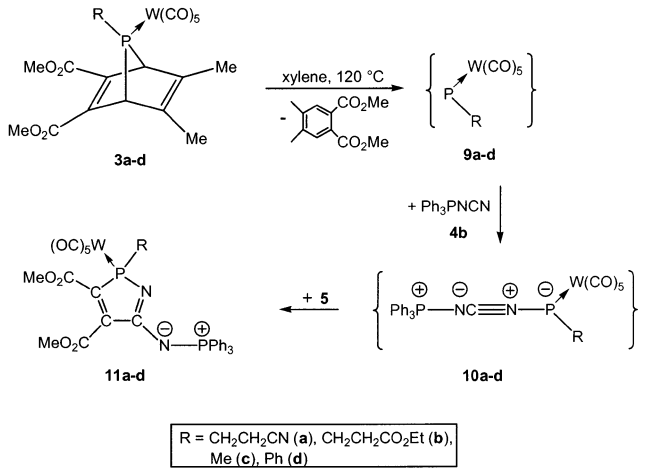
Scheme 3. Unselective Synthesis of Multifunctional 2*H*-1,2-Azaphosphole Complex 6



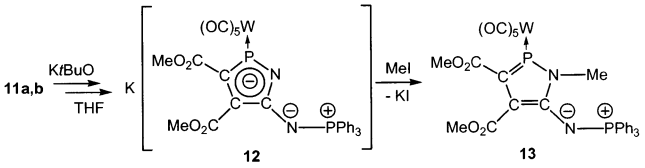
Scheme 4. Selective Synthesis of Multifunctional 2*H*-1,2-Azaphosphole Complexes 11



amino-substituted derivatives. Therefore, we decided to carry out a comparative study using the 7-phosphanorbornadiene complexes **3a**,[15] **3b**,[13] and **3c**,**d**,[17] the carbonitrile derivative **4b**,[18] and DMAD (**5**). Our assumptions on the reaction course are shown in Scheme 4 and are based on the intermediate formation of the terminal phosphanediyl complexes **9a**−**d**, which then react with carbonitriles to the nitrilium phosphane-ylide complexes **10a**−**d**. These then undergo [3+2] cycloaddition reactions with DMAD, thus yielding finally 2*H*-1,2-azaphosphole complexes **11a**−**d**.

First attempts to liberate the 2*H*-1,2-azaphosphole ligands from the complexes **11a**−**d** using bis(diphenylphosphino)ethane (DPPE) in *o*-xylene at 140 °C (cf. ref 13) failed. This thermal stability of **11a**−**d** is in marked contrast to that of the corresponding bulky *P*-bis(trimethylsilyl)methyl-substituted 2*H*-1,2-azaphosphole complex **11e**,[16] which yields the noncoordinated

Scheme 5. Generation and Reaction of a Presumably Formed 1,2-Azaphospholide Complex



2*H*-1,2-azaphosphole under the same reaction conditions.[20] Initial studies of cleavage reactions of the exocyclic P−C bonds of 2*H*-1,2-azaphosphole complexes **11a** and **11b** showed instantaneous reactions of **11a**,**b** with potassium *tert*-butanolate (KO*t*Bu) at ambient temperature (cf. refs 13. 14), accompanied by a color change from bright yellow to dark red and leading to a mixture of products. Repeating the reactions under the same conditions (0 °C) but with a longer reaction time and warming up to ambient temperature changed the situation as shown by ^{31}P NMR spectroscopic monitoring. In each case, we now observed one major product (ca. 75%), having a set of resonances of an AB-type, i.e., **11a**/KO*t*Bu: δ = 125.0 and 19.7 (**12**) and **11b**/KO*t*Bu: δ = 127.9 (^4J(P,P) = 7.6 Hz) and 15.4 (^4J(P,P) = 6.7 Hz) (**12**). In the latter case, a phosphorus−tungsten coupling of 302.8 Hz was observed additionally, thus lending further support to the structural assignment of **12** as the first 1,2-azaphospholide derivative, a situation in which the phosphorus is expected to be approximately sp^2-hybridized and the negative charge is mainly localized at the nitrogen (Scheme 5). Despite some minor differences in the phosphorus NMR data, and although we have no firm proof, we assume that the main products were identical in both reactions. Subsequent quenching of the reaction solutions with an excess of methyl iodide led again to a color change from dark red to dark yellow and the precipitation of a solid. The formation of a new major product was spectroscopically detected, i.e., **11b**/KO*t*Bu/MeI: δ = 153.2 (A-part, ^1J(W,P) = 315.6 Hz) (**13**); the resonance of the B-part was obscured by other resonances in the range 15−20 ppm. We conclude that a reaction of **12** with methyl iodide probably led in the first step to *N*-methylation of the azaphospholide nitrogen atom and metal salt formation (Scheme 5). Attempts to separate and purify compound **13** by column chromatography have so far failed; therefore, only phosphorus NMR data are available.

To check the assumed reaction course—exocyclic P,C-bond cleavage and methylation reaction—we turned our attention to a different but related N,P,C-heterocycle, the 2*H*-1,3,2-diazaphosphole ring system. Additionally we focused on mono-ester-functionalized derivatives, thus (hopefully) avoiding side reactions. Therefore, we synthesized tungsten complex **14** via a two-component reaction using complex **3b** and 2 equiv of dimethyl cyanamide in toluene at 65 °C with a catalytic amount of copper(I) chloride (Scheme 6). Interestingly, we obtained only the 2*H*-1,3,2-regioisomer, thus also showing that regioisomer formation largely depends on the reaction temperature! (cf. ref 7).

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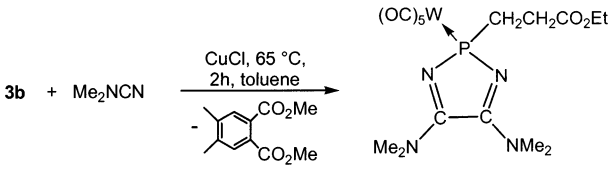
Table 1. Ab Initio Geometries (bond lengths), Relative Energies, and NICS Values of Lithium and Potassium Azaphospholides[a]

Compound		Bond lengths [Å]										NICS	Rel.E.
LiC_3H_3NP		Li–N	Li–P	Li–C2	Li–C4	Li–C5	N-C2	N-C5	P-C2	C4-C5	P-C4	SCF[c]	[kJ/mol]
A	[a]	2.075	2.483	2.136	2.255	2.121	1.376	1.369	1.768	1.403	1.769	-14.89	+14.04
	[b]	2.078	2.455	2.150	2.244	2.120	1.329	1.354	1.750	1.378	1.764		
		Li–N	Li–P	Li–C3	Li–C4	Li–C5	N-P	N-C5	P-C3	C4-C5	C3-C4		
B	[a]						1.691	1.354	1.752	1.407	1.410	-12.38	
	[b]						1.669	1.314	1.736	1.403	1.388		
C	[a]	2.110	2.373	2.276	2.219	2.114	1.705	1.365	1.764	1.410	1.412	-15.13	0.00
	[b]	2.104	2.350	2.275	2.221	2.122	1.674	1.324	1.743	1.405	1.395		
D	[a]	1.825	2.490				1.719	1.360	1.733	1.394	1.406	-13.42	+19.26
	[b]	1.796	2.587				1.692	1.326	1.710	1.385	1.393		
KC_3H_3NP		K–N	K–P	K–C3	K–C4	K–C5	N-P	N-C5	P-C3	C4-C5	C3-C4		Rel.E.
E	[a]	2.775	3.053	3.073	3.006	2.827	1.702	1.363	1.759	1.406	1.410	-13.20	0.00
	[b]	2.837	3.104	3.184	3.125	2.925	1.673	1.319	1.738	1.403	1.391		
F	[a]	2.528	3.054				1.712	1.361	1.737	1.398	1.405	-12.86	+15.56
	[b]	2.563	3.098				1.686	1.318	1.720	1.395	1.386		

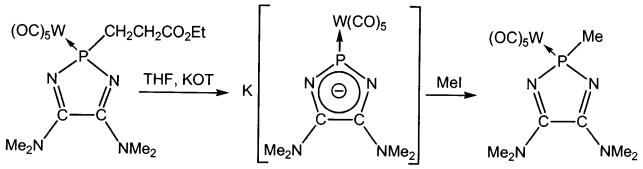
[a] [a]: rMP2(fc), [b]: rHF, [c]: GIAO-SCF//rMP2(fc)/6-311++g(2d,p), basis set [a,b]: 6311++g(2d,p) on all atoms. All geometries have been characterized by a number of zero imaginary frequencies using GAUSSIAN 98. Energies are zero-point-corrected (sums of electronic and zero-point energies).

Scheme 6. Synthesis of Mono-ester-Functionalized 2*H*-1,3,2-Diazaphosphole Complex 14



14

Scheme 7. Generation and Methylation of Intermediately Formed 1,3,2-Diazaphospholide Complex 15



14 15 16

Adding small amounts of KO*t*Bu (5 equiv) to a THF solution of complex **14** at 0 °C (period of 80 min) and warming to ambient temperature (18 h) resulted in a color change from yellow to dark red and the formation of complex **15** showing a ^{31}P-resonance at 117.5 ppm and a very low phosphorus−tungsten coupling of 172.2 Hz; such values are similar to those observed for phospholide complexes (cf. ref 21). The crude product mixture was analyzed with CI (methane) mass spectra and the molecular ion was observed, thus providing evidence for the nature of **15** as a new 1,3,2-diazaphospholide complex (Scheme 7). Adding an excess of methyl iodide to such a solution resulted in the formation of a new major product with a ^{31}P-resonance at 126.6 and a phosphorus−tungsten coupling of 269.5 Hz. Surprised by this result—we had expected a significantly higher phosphorus−tungsten coupling constant value for an *N-methylated* species (!)—we decided to synthesize the *P*-methyl-substituted 2*H*-1,3,2-diazaphosphole complex **16** using the same reaction protocol as for **14**. In this case only the 2*H*-1,3,2-regioisomer was isolated. Pure complex **16** was then used as authentic sample, thus providing strong evidence for the nature of the product formed using the system KO*t*Bu/methyl iodide and **14**. At the moment, we do not understand why *P*-methylation is preferred in this case.

It should be noted that *N*-methylation has been described earlier for noncoordinated 1,3,2-diazaphospholide derivatives with different *C*-substituents (cf. ref 22). Although the general quest of *N*- vs *P*-methylation remains open, we take the outcome of this additional study as further support for 1,2-azaphospholide formation in the case of the reactions of **11a**,**b** → **12**.

Ab Initio Calculations. To shed more light on the quest for the 1,2-azaphospholides, we also investigated monomers of [LiC_3H_3NP]: the free 1,2-azaphospholide (**B**), two isomers of lithium and potassium 1,2-azaphospholides (**C**−**F**), and, for comparison, the η^5-lithium 1,3-azaphospholide (**A**), first calculated by Veszprémi et al.,[9] by ab initio calculations using HF and MP2/6-311++G-(2d,p) levels of theory (Tables 1 and 2).

Compounds **C** and **E** have structures with equalized C4−C5/C3−C4 bond lengths and SCF-NICS[23,24] values higher than (**C**) or similar to (**E**) that of the correspond-

Table 2. Ab Initio Geometries (bond angles, dihedral angles) of Lithium and Potassium Azaphospholides[a]

Compound		Bond angles [deg]					Dihedral angles [deg]			
LiC_3H_3NP		C2PC4	C2NC5	NC5C4	PC4C5	PC2N	C5NC2P	NC5C4P	NC2PLi	C5C4PLi
A	[a]	86.95	109.34	115.86	111.24	116.53	0.40	3.33	58.79	-56.57
	[b]	87.10	110.37	115.97	110.38	116.11	1.74	3.04	58.33	-57.26
		NPC3	PNC5	NC5C4	C3C4C5	PC3C4	C4C5NP	C5C4C3P	C4C3PLi	C5NPLi
B	[a]	94.30	109.15	117.30	110.52	108.73	-0.03	0.01		
	[b]	93.68	110.23	117.06	110.25	108.79	-0.03	0.01		
C	[a]	92.47	110.86	115.80	110.73	109.91	-4.31	2.21	-58.56	63.40
	[b]	92.36	111.78	115.72	110.26	109.69	-4.45	1.15	-58.77	64.27
D	[a]	93.28	109.94	115.25	112.35	109.18	-0.01	-0.06	0.64	-179.51
	[b]	93.17	110.33	115.73	111.42	109.35	0.02	-0.03	0.58	-179.48
KC_3H_3NP		NPC3	PNC5	NC5C4	C3C4C5	PC3C4	C4C5NP	C5C4C3P	C4C3PK	C5NPK
E	[a]	93.28	110.03	116.36	110.85	109.32	-3.35	2.08	-65.41	74.20
	[b]	93.07	110.84	116.48	110.26	109.24	-3.37	1.07	-65.89	76.91
F	[a]	94.01	109.14	116.11	111.93	108.82	0.01	-0.03	0.87	-178.49
	[b]	93.68	109.84	116.45	111.13	108.90	0.01	-0.02	0.74	-178.81

[a] [a]: rMP2(fc), [b]: rHF, basis set [a,b]: 6311++g(2d,p) on all atoms. All geometries have been characterized by a number of zero imaginary frequencies using GAUSSIAN 98. Energies are zero-point-corrected (sums of electronic and zero-point energies).

ing lithium 1,3-azapholide isomer reported by Veszprémi et al.[9] The SCF-NICS value of **C** is slightly enhanced as compared with **A**, and furthermore, **C** is significantly lower in energy (**A**: +14.04 [kJ/mol]) (Table 1). According to the Li/K ring atom distances, species **C** and **E** exhibit slightly displaced pentahapto-bonded metal ions toward the N−C5 unit, indicating a negative charge at nitrogen (Table 1). This corresponds with the rMP2(fc)-NPA charges[25] of **C** and **E** (Table 3). The lithium and potassium ions are at distances of 1.80 Å (**A** and **C**) and 2.56 Å (**E**) above the rings, calculated as distances to the nonweighted mean of the heavy ring atoms (the points of NICS calculation).

It is also noteworthy that **A**, **C**, and **E** are puckered rings with a phosphorus in an envelope-type position pointing away from the lithium (Table 2). Despite this geometrical situation, **A**, **C**, and **E** have higher NICS values than the bare anion **B**, which is more or less perfectly planar (Table 2). This finding seems to contradict the observation by Goldfuss and Schleyer[26] that planar group 14 metallolyl anions $C_4H_4EH^-$ (E = C, Si, Ge, Sn, Pb) exhibited more negative NICSs than the anions in the nonplanar geometries (E = Si, Ge, Sn, Pb).

Table 3. rMP2(fc)-NPA Charge Distribution

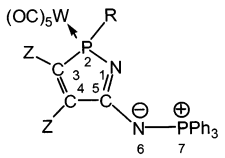
	compound						
charge at	**A**	**B**	**C**	**D**	**E**		**F**
Li	+0.91	Li	+0.91	+0.93	K	+0.96	+0.96
N	−0.58	N −0.87	−0.89	−1.05	N	−0.89	−0.99
P	+0.41	P +0.51	+0.59	+0.49	P	+0.55	+0.45
C2	−0.50	C3 −0.70	−0.72	−0.63	C3	−0.71	−0.64
C4	−0.72	C4 −0.36	−0.38	−0.29	C4	−0.37	−0.30
C5	−0.15	C5 −0.08	−0.14	−0.05	C5	−0.13	−0.06

Discussion of Selected NMR Spectroscopic Data. The analytical data including elemental analyses, MS spectrometric data, and IR and NMR spectroscopic data readily confirm the molecular structures of all compounds reported here, which were separated and purified by column chromatography at low temperature and subsequent crystallization in most cases. NMR data are discussed here; for further analytical data see the Experimental Section. The most significant NMR data of the 2*H*-1,2-azaphosphole ring atoms of complexes **11a**−**d** are collected in Table 4.

As expected, the ^{31}P NMR resonances showed tungsten−phosphorus couplings, but no phosphorus−phosphorus couplings, as was recently observed in the case of complex **11e**.[16] The $^{13}C\{^1H\}$ NMR spectra displayed three resonances for the 2*H*-1,2-azaphosphole ring with

(21) Holand, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1984**, *106*, 826.
(22) Karaghiosoff, K.; Klehr, H.; Schmidtpeter, A. *Chem. Ber.* **1986**, *119*, 410.
(23) von Ragué Schleyer, P.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
(24) von R. Schleyer, P., et al. proposed the absolute isotropic shielding at the "nonweighted mean of the heavy atom coordinates" (nucleus-independent chemical shift) of a heterocycle as a measure of the aromaticity of the ring. The points for the NICS value calculation have been constructed using the following routine with GAUSSIAN 98 and GAUSS-View: Without changing angles or bond lengths of the optimized geometry delete all substituents of the ring atoms and replace every heteroatom by carbon. Let GAUSSIAN find the nonweighted mean of this "dummy-ring" by a check of coordinates (using the guess=only keyword). Place a ghost atom at the zero-point of the coordinate system which is the center of mass of the dummy-ring. Let GAUSSIAN create a *z*-matrix of both the dummy-ring including the ghost atom and the optimized heterocycle. Add a ghost atom to the *z*-matrix of the optimized heterocycle at the position that comes out of the *z*-matrix of the dummy-ring. Perform a NMR calculation of the optimized heterocycle including the ghost atom.
(25) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 1736.
(26) Goldfuss, B.; von R. Schleyer, P. *Organometallics* **1997**, *16*, 1543.

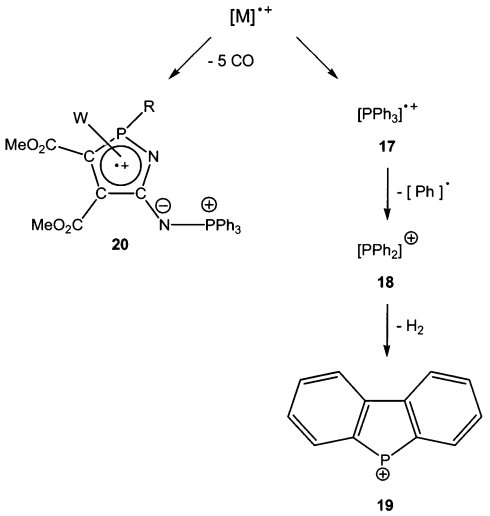
Table 4. Selected NMR Spectroscopic Data[a] of the 2*H*-1,2-Azaphosphole Complexes 11a−e



compd	δ ^{31}P$^{2/7}$	^{1}J(W,P)	δ^{13}C^{3}	^{1+4}J(P,C^{3})	δ^{13}C^{4}	^{2+3}J(P$^{2/7}$,C^{4})	δ^{13}C^{5}	^{2+3}J(P,C^{5})
11a	79.6, 21.3	255.1	148.4	5.8	150.8	25.8, *b*	169.2	*b*
11b	81.6, 20.6	255.9	149.5	*b*	161.8	21.1, 2.4	168.5	*b*
11c	76.2, 20.4	246.9	151.8	9.7	149.1	26.2, *b*	162.0	2.3
11d	81.6, 20.9	253.1	150.0	6.7	148.2	26.1, *b*	169.1	5.8
11e[16]	85.8, 14.7	249.6	163.1	14.0	149.0	48.1, 25.8	153.3	*b*

[a] In $CDCl_3$; δ in ppm; J in Hz. [b] Not resolved.

Scheme 8. Fragmentation of the Molecular Radical Cations of 11a−d



different phosphorus−carbon coupling constant magnitudes. The assignment of the resonances was made according to a recent publication.[16] Apart from the typical small $|J(^{31}P,^{13}C)|$ values for the C^5 atoms, we again observed that the phosphorus−carbon coupling constant magnitude values of the C^4 atoms were always greater than those of the C^3 atoms, although the latter are directly bonded to phosphorus.

The signals of the molecular radical cations of **11a−d** range from lower 1% to 16% relative abundance. As a general feature, significant intensities can be observed for the triphenylphosphine fragment **17** and its degradation products **18** and **19** in the lower mass range.[27] In the upper range the spectra are dominated by fragments that all display the typical isotopic distribution for tungsten. They are formed by successive loss of carbon monoxide. The complete elimination of (pentacarbonyl)tungsten was not observed. Elimination of CO is influenced by the substituent R. Thus, fragment radical cation **20** represents the base peak in the spectrum of **11d**, and it has a relative abundance of 92% in the spectrum of **11a**. The most stable decarbonylation product of **11b** and **11c** is not **20** but the fragment radical cation $[M - 4CO]^{+\bullet}$ or $[M - 2CO]^{+\bullet}$, respectively. In both cases fragment **20** is displayed with a relative abundance of 14% for **11c** and 5% for **11b** (Scheme 8).

We were able to confirm the constitutions of complexes **11a−d** by X-ray single-crystal structure analyses (Figures 1−4 and Tables 5−7).

(27) Miller, J. Ph.D. Thesis, Cambridge University, 1996.

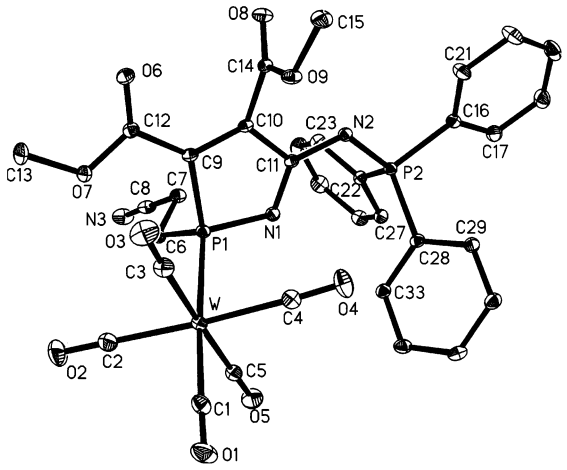


Figure 1. Molecular structure of **11a** in the crystal (ellipsoids represent 50% probability levels; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [deg]: N2−C11 1.344(3), N1−P1−C9 94.34(10), N1−P1−C6 105.04(11), C6−P1−C9 108.47(11), C11−N1−P1 110.29(15), C10−C9−P1 106.34(16), C9−C10−C11 112.7-(2), N1−C11−C10 115.1(2).

The 2*H*-1,2-azaphosphole rings of complexes **11a−d** showed no unusual bond lengths involving the ring atoms and those atoms bonded externally to them. In all cases the 2*H*-1,2-azaphosphole rings are approximately planar (largest mean deviation 0.047 Å in **11a**), and the groups at the phosphorus (P1) in all cases adopt the preferred relative orientation toward the tungsten center and thus toward the ring, as already reported for other structures of related phosphorus heterocycle complexes. The absolute torsion angles of $N-C-N_{endo}-P_{endo}$ are not larger than 20.5° (in **11c**); this should in all cases enable electronic interactions between the ring system and the substituent. It is remarkable that there is no correlation between these values and the nature of the *P*-substituents. In all cases the $NPPh_3$ group adopts an *s-cis* configuration with respect to the C−N(2) bond.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of deoxygenated dry nitrogen, using standard Schlenk techniques with conventional glassware, and solvents were dried according to standard procedures. NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz for ^{1}H; 50.3 MHz for ^{13}C; 81.0 MHz for ^{31}P) using [D]chloroform and [D_6]benzene as solvent and

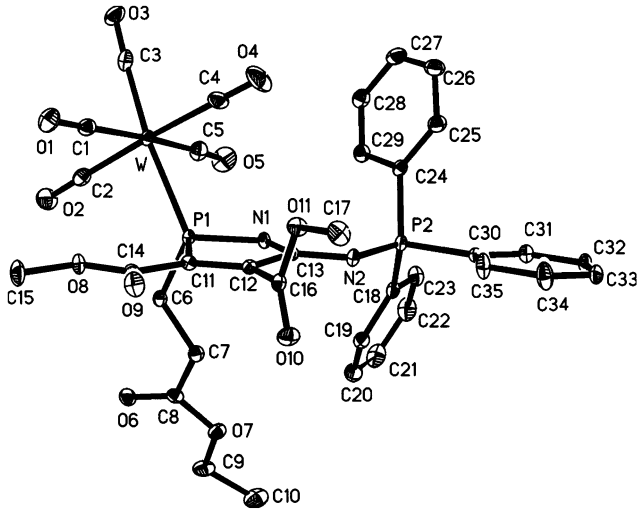


Figure 2. Molecular structure of one of the two independent molecules of **11b** in the crystal (ellipsoids represent 30% probability levels; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [deg]: N2−C13 1.345(3) (1.341(3)), N1−P1−C11 94.13(10) (94.32(10)), N1−P1−C6 105.76(11) 105.17(11), C6−P1−C11 106.09(11) 108.01(11), C13−N1−P1 110.37(16) 110.30(16), C12−C11−P1 107.01(17) (106.47(18)), C11−C12−C13 112.7(2) (112.7(2)), N1−C13−C12 115.5(2) (115.5(2)).

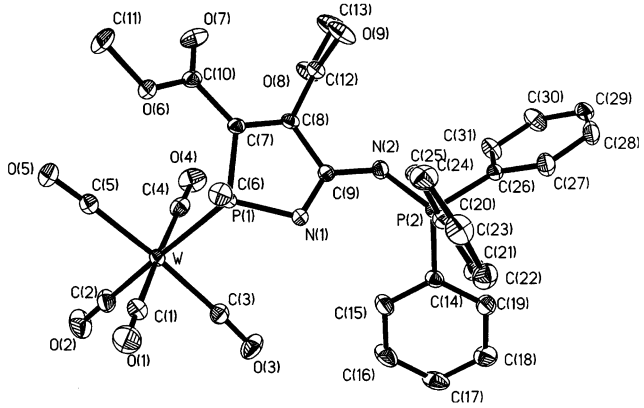


Figure 3. Molecular structure of **11c** in the crystal (ellipsoids represent 50% probability levels; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [deg]: N2−C9 1.343(2), N1−P1−C7 94.26(8), N1−P1−C6 105.15(9), C6−P1−C7 104.62(9), C9−N1−P1 110.41(13), C8−C7−P1 107.37(13), C7−C8−C9 112.40(17), N1−C9−C8 115.30(16).

internal standard; shifts are given relative to external tetramethylsilane (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P); only coupling constant magnitudes are given. Electron impact (EI) (70 eV) chemical ionization (CI) (ammonia or methane) and fast atom bombardement (FAB) (Xenon) mass spectra were recorded on a Finnigan MAT-8430 double-focusing mass spectrometer. Infrared spectra were recorded on a Biorad FT-IR 165 (selected data given). Ultraviolett/vis spectra were recorded on a Hewlett-Packard HP 8452. Melting points were obtained on a Büchi 535 capillary apparatus. Elemental analyses were performed using a Carlo Erba analytical gaschromatograph. The *κP*-notation in the nomenclature is intended to differentiate between P- and N-coordination of the appropriate heterocycle to the metal.

General Procedure for the Preparation of Complexes 11a−d. To a solution of 7-phosphanorbornadiene complexes **3a−d** (1 mmol each), dissolved in *o*-xylene (6 mL), carbonitrile **4b** (1 mmol) and DMAD **5** (1 mmol) were added and the solutions heated at 120 °C for 45 min with slow stirring. All volatile components were removed in vacuo (ca. 0.01 mbar) and the products separated by low-temperature column chromatography (SiO_2, −10 °C, 10 × 2 cm, *n*-pentane/diethyl ether, 1:1). Evaporation of the second fractions yielded complexes **11a−d** as yellow solids.

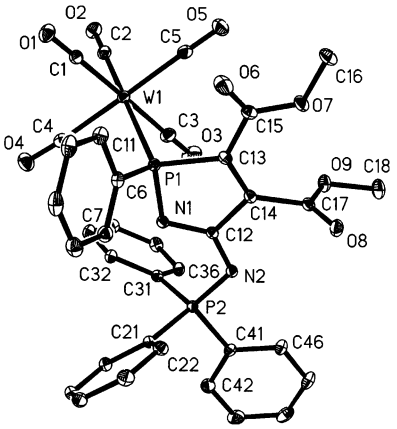


Figure 4. Molecular structure of one of the two independent molecules of **11d** in the crystal (ellipsoids represent 50% probability levels; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [deg]: N2−C12 1.344(2) 1.340(2)), N1−P1−C13 94.00(9) 93.94(8)), N1−P1−C6 105.82(9) 105.10(9), C6−P1−C13 106.54(9) 106.06(9)), C12−N1−P1 110.80(13) 110.87(13)), C14−C13−P1 107.37(14) 106.99(14)), C12−C14−C13 111.60(17) 112.51(17)), N1−C12−C14 115.47(16) 115.06(16).

{**[3,4-Bis(methoxycarbonyl)-2-(2-cyanoethyl)-5-(*N*-triphenylphosphonioiminoyl)-2*H*-1,2-azaphosphole-*κP*]-pentacarbonyltungsten(0)**} **(11a).** Yield: 650 mg (78%); mp 152 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.51 (m_c, 2H, CH_2CH$_2$CN), 2.23 (m_c, 2H, CH$_2$CH_2CN), 3.77 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 7.48 (m_c, 7H, Ph), 7.58 (m_c, 3H, Ph), 7.79 (m_c, 5H, Ph); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 11.2 (d, ^2J(P,C) = 3.2 Hz, −CH$_2$*C*H$_2$-CN), 30.8 (d, ^1J(P,C) = 9.8 Hz, −*C*H$_2$CH$_2$CN), 52.7 (s, O*C*H$_3$), 52.8 (s, O*C*H$_3$), 118.2 (d, ^3J(P,C) = 13.9 Hz, −*C*N), 126.1 (d, ^1J(P,C) = 100.7 Hz, *ipso*-Ph), 128.7 (d, ^3J(P,C) = 12.6 Hz, *meta*-Ph), 132.9 (d, ^4J(P,C) = 2.9 Hz, *para*-Ph), 133.2 (d, ^2J(P,C) = 10.1 Hz, *ortho*-Ph), 148.4 (d, ^1J(P,C) = 5.8 Hz, P*C*C), 150.8 (d, ^2J(P,C) = 25.8 Hz, PC*C*), 161.5 (d, ^2J(P,C) = 12.2 Hz, *C*O$_2$-CH$_3$), 164.7 (d, ^3J(P,C) = 16.1 Hz, *C*O$_2$CH$_3$), 169.2 (s, PN*C*), 195.4 (d, ^2J(P,C) = 7.5 Hz, *cis*-*C*O), 198.9 (d, ^2J(P,C) = 23.3 Hz, *trans*-*C*O); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 21.3 (s, *P*Ph$_3$), 79.6 (s, ^1J(W,P) = 255.1 Hz); UV/vis (CH_3CN) λ (lg ϵ) = 230 (4.99), 248 (4.63), 260 (4.44), 270 (4.18), 280 (3.98), 324 (3.90), 346 (3.87), 376 (3.63), 406 (3.36); IR (KBr) $\tilde{\nu}$ 2075 (vs, CO), 1983 (vs, CO), 1945 (s, CO), 1921 (s, CO), 1907 (s, CO), 1742 (vs, CO_2), 1717 (vs, CO_2) cm^{-1}; MS (EI, ^{184}W); *m*/*z* 853 (6) [M]$^{+\bullet}$, 797 (32) [M − 2CO]$^+$, 713 (90) [M − 5CO]$^+$, 262 (58) [PPh$_3$], 183 (100) [PPh$_2$]$^+$, 73 (46) [Si(CH$_3$)$_3$]; MS (pos.-CI(NH$_3$), ^{35}Cl, ^{184}W); *m*/*z* 958 (39) [M + H]$^+$, 635 (74) [M + H − W(CO)$_5$]$^+$, 263 (100) [PPh$_3$ + H]$^+$. Anal. Calcd. for $C_{33}H_{25}N_3O_9P_2W$: C, 46.45; H, 2.95; N, 4.92. Found: C, 47.69; H, 3.26; N, 4.96.

{**[3,4-Bis(methoxycarbonyl)-2-(2-ethoxycarbonylethyl)-5-(*N*-triphenylphosphonioiminoyl)-2*H*-1,2-azaphosphole-*κP*]pentacarbonyltungsten(0)**} **(11b).** Yield: 782 mg (87%); mp 113 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.16 (t, ^3J(H,H) = 7.1 Hz, 3H, CO$_2$CH$_2$CH_3), 1.70 (m_c, 2H, PCH_2CH$_2$CO$_2$Et), 2.22 (m_c, 2H, PCH$_2$CH_2CO$_2$Et), 3.35 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 3.98 (m_c, 2H, CO$_2$CH_2CH$_3$), 7.38 (m_c, 7H, Ph), 7.48 (m_c, 3H, Ph), 7.70 (m_c, 5H, Ph); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.1 (s, CH$_2$*C*H$_3$), 27.8 (d, ^2J(P,C) = 4.3 Hz, PCH$_2$*C*H$_2$CO$_2$Et), 30.0 (d, ^1J(P,C) = 23.3 Hz, P*C*H$_2$CH$_2$CO$_2$Et), 52.5 (s, O*C*H$_3$), 52.6 (s, O*C*H$_3$), 60.6 (s, O*C*H$_2$CH$_3$), 126.5 (d, ^1J(P,C) = 100.7 Hz, *ipso*-Ph), 128.6 (d, ^3J(P,C) = 12.6 Hz, *meta*-Ph), 132.6 (d, ^4J(P,C) = 2.8 Hz, *para*-Ph), 133.2 (d, ^2J(P,C) = 10.1 Hz, *ortho*-Ph), 149.5 (s, P*C*C),

Table 5. Crystal Data and Structure Refinement of Complexes 11a−d

	11a·$3CH_2Cl_2$	**11b**	**11c**	**11d**·$3/2CH_2Cl_2$
formula	$C_{36}H_{31}Cl_6N_3O_9P_2W$	$C_{35}H_{30}N_2O_{11}P_2W$	$C_{31}H_{24}N_2O_9P_2W$	$C_{37}H_{29}Cl_3N_2O_9P_2W$
M_r	1108.13	900.40	814.31	1003.77
cryst size (mm)	0.49 × 0.37 × 0.29	0.24 × 0.18 × 0.05	0.24 × 0.23 × 0.17	0.47 × 0.42 × 0.34
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
unit cell dimens				
a (Å)	13.388(2)	13.0228(8)	9.0630(12)	11.8945(11)
b (Å)	13.458(2)	13.5518(8)	21.616(3)	12.8234(12)
c (Å)	14.298(2)	24.1578(16)	16.695(2)	27.084(2)
α (deg)	68.213(6)	77.715(5)	90	100.416(4)
β (deg)	66.518(6)	74.638(5)	99.522(5)	91.903(4)
γ (deg)	77.182(6)	63.712(5)	90	100.960(4)
V (Å^3)	2185.8(6)	3663.4(4)	3225.6(8)	3979.1(6)
Z	2	4	4	4
D_x (Mg m^{-3})	1.684	1.633	1.677	1.676
μ (mm^{-1})	3.136	3.302	3.736	3.240
transmns	0.327−0.528	0.564−0.746	0.552−0.746	0.368−0.494
F(000)	1092	1784	1600	1980
T(K)	133(2)	143(2)	133(2)	133(2)
$2\theta_{max}$	60	60	60	60
no. of reflns				
measured	43 807	77 673	61 191	71 415
unique	12 695	21 328	9451	23 126
R_{int}	0.0355	0.0478	0.0823	0.0232
no. of params	516	925	409	984
no. of restraints	78	144	285	144
R_w (F^2, all reflns)	0.0773	0.0536	0.0643	0.0552
R (F, $I > 2\sigma(I)$)	0.0289	0.0275	0.0264	0.0230
S	1.06	0.92	1.03	1.02
max $\Delta\rho$ (e Å^{-3})	1.81	1.61	2.14	1.15

Table 6. Selected Bond Lengths [Å] of the 2*H*-1,2-Azaphosphole Complexes 11a−e; P−W, P−C_{exo}, and Ring Bonds

compd	P−W	P−C_{exo}	P−C	P−N	C=C	N=C	C−C
11a	2.4947(7)	1.833(2)	1.826(2)	1.685(2)	1.344(3)	1.321(3)	1.496(3)
11b[a]	2.4932(7)	1.826(2)	1.825(2)	1.687(2)	1.331(3)	1.311(3)	1.495(3)
	2.4891(7)	1.825(3)	1.823(2)	1.684(2)	1.334(3)	1.311(3)	1.499(3)
11c	2.4941(6)	1.821(2)	1.8190(19)	1.6932(16)	1.338(3)	1.317(2)	1.501(2)
11d[a]	2.5036(5)	1.821(2)	1.829(2)	1.6825(16)	1.347(3)	1.317(3)	1.507(3)
	2.5110(5)	1.826(2)	1.833(2)	1.6851(16)	1.343(3)	1.321(2)	1.499(3)
11e[16]	2.5384(4)	1.8312(16)	1.8345(16)	1.7005(14)	1.345(2)	1.311(2)	1.502(2)

[a] Two independent molecules.

Table 7. Torsion Angles [deg] of 2*H*-1,2-Azaphosphole Complexes 11a−e

compd	torsion angle N−C−N_{endo}−P_{endo}
11a	2.4
11b[a]	3.2
	1.6
11c	−20.5
11d[a]	2.0
	−0.3
11e[16]	−18.9

[a] Two independent molecules.

161.8 (dd, ^1J(P,C) = 21.1 Hz, ^4J(P,C) = 2.4 Hz, PC*C*), 161.9 (d, ^2J(P,C) = 3.0 Hz, *C*O_2CH_3), 165.1 (d, ^3J(P,C) = 15.3 Hz, *C*O_2CH_3), 168.5 (s, PN*C*), 171.9 (d, ^3J(P,C) = 12.8 Hz, *C*O_2Et), 195.8 (d, ^2J(P,C) = 7.6 Hz, *cis*-*C*O), 199.6 (d, ^2J(P,C) = 22.1 Hz, *trans*-*C*O); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 20.6 (s, *P*Ph_3), 81.6 (s, ^1J(W,P) = 249.8 Hz); UV/vis (CH_3CN) λ (lg ϵ) = 230 (5.00), 248 (4.66), 260 (4.46), 270 (4.17), 282 (3.92), 294 (3.88), 326 (3.90), 368 (3.69), 390 (3.46); IR (KBr) $\tilde{\nu}$ 2073 (vs, CO), 1962 (vs, CO), 1946 (s, CO), 1920 (s, CO), 1743 (vs, CO_2), 1720 (vs, CO_2) cm^{-1}; MS (EI, ^{184}W); *m*/*z* 899 (2) [M − H]$^{+\bullet}$, 872 (60) [M − CO]$^+$, 844 (100) [M − 2CO]$^+$, 760 (8) [M − 5CO]$^+$, 262 (96) [PPh_3], 183 (60) [PPh_2]$^+$. Anal. Calcd for $C_{35}H_{30}N_2O_{11}P_2W$: C, 46.69; H, 3.36; N, 3.11. Found: C, 46.67; H, 3.44; N, 3.07.

{**[3,4-Bis(methoxycarbonyl)-2-methyl-5-(*N*-triphenylphosphonioiminoyl)-2*H*-1,2-azaphosphole-κ*P*]pentacarbonyltungsten(0)**} **(11c).** Yield: 660 mg (81%); mp 161 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.67 (d, ^1J(P,H) = 7.6 Hz, 3H, PC*H*$_3$), 3.83 (s, 3H, OC*H*$_3$), 4.01 (s, 3H, OC*H*$_3$), 7.45 (m_c, 7H, Ph), 7.56 (m_c, 3H, Ph), 7.76 (m_c, 5H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 21.4 (d, ^1J(P,C) = 26.2 Hz, P*C*H$_3$), 52.6 (s, O*C*H$_3$), 52.7 (s, O*C*H$_3$), 126.9 (d, ^1J(P,C) = 100.7 Hz, *ipso*-Ph), 128.6 (d, ^3J(P,C) = 12.5 Hz, *meta*-Ph), 132.6 (d, ^4J(P,C) = 2.7 Hz, *para*-Ph), 133.3 (d, ^2J(P,C) = 10.2 Hz, *ortho*-Ph), 149.1 (d, ^2J(P,C) = 26.2 Hz, PC*C*), 151.8 (d, ^1J(P,C) = 9.7 Hz, P*C*C), 162.0 (d, ^2J(P,C) = 2.3 Hz, PN*C*), 165.6 (d, ^3J(P,C) = 15.8 Hz, *C*O_2CH_3), 167.6 (d, ^2J(P,C) = 8.6 Hz, *C*O_2CH_3), 196.1 (d, ^2J(P,C) = 7.6 Hz, *cis*-*C*O), 200.1 (d, ^2J(P,C) = 21.5 Hz, *trans*-*C*O); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 20.4 (s, *P*Ph_3), 76.2 (s, ^1J(W,P) = 246.9 Hz); UV/vis (CH_3CN) λ (lg ϵ) = 230 (4.99), 240 (4.83), 248 (4.64), 260 (4.44), 272 (4.07), 284 (3.85), 308 (3.80), 326 (3.85), 344 (3.82); IR (KBr) $\tilde{\nu}$ 2070 (vs, CO), 1989 (vs, CO), 1943 (s, CO), 1933 (s, CO), 1916 (s, CO), 1747 (vs, CO_2), 1724 (vs, CO_2) cm^{-1}; MS (EI, ^{184}W); *m*/*z* 814 (10) [M]$^{+\bullet}$, 758 (22) [M − 2CO]$^+$, 730 (40) [M − 3CO]$^+$, 702 (95) [M − 4CO]$^+$, 262 (98) [PPh_3]$^+$, 183 (100) [PPh_2]$^+$. Anal. Calcd for $C_{31}H_{24}N_2O_9P_2W$: C, 45.72; H, 2.97; N, 3.44. Found: C, 45.58; H, 3.13; N, 3.35.

{**[3,4-Bis(methoxycarbonyl)-2-phenyl-5-(*N*-triphenylphosphonioiminoyl)-2*H*-1,2-azaphosphole-κ*P*]pentacarbonyltungsten(0)**} **(11d).** Yield: 460 mg, (58%); mp 67 °C (dec); ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 3H, OC*H*$_3$), 3.91 (s, 3H, OC*H*$_3$), 7.08 (m_c, 5H, Ph), 7.40 (m_c, 3H, Ph), 7.45 (m_c, 7H, Ph), 7.78 (m_c, 5H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 52.5 (s, O*C*H$_3$), 52.8 (s, O*C*H$_3$), 126.8 (d, ^1J(P,C) = 100.6 Hz, *ipso*-Ph(Ph_3P)), 128.0 (d, ^2J(P,C) = 10.3 Hz, *ortho*-Ph), 128.8 (d, ^3J(P,C) = 12.6 Hz,

meta-Ph(Ph_3P)), 130.2 (s, *para*-Ph), 130.4 (d, ^3J(P,C) = 12.4 Hz, *meta*-Ph), 132.7 (d, ^4J(P,C) = 2.8 Hz, *para*-Ph(Ph_3P)), 133.4 (d, ^2J(P,C) = 10.2 Hz, *ortho*-Ph(Ph_3P)), 134.6 (d, ^1J(P,C) = 39.7 Hz, *ipso*-Ph), 148.2 (d, ^2J(P,C) = 26.1 Hz, P*C*C), 150.0 (d, ^1J(P,C) = 6.7 Hz, P*C*C), 162.0 (d, ^3J(P,C) = 14.8 Hz, *C*O_2CH_3), 165.5 (d, ^3J(P,C) = 16.2 Hz, *C*O_2CH_3), 169.1 (d, ^2J(P,C) = 5.8 Hz, PN*C*), 196.3 (d, ^2J(P,C) = 7.5 Hz, *cis*-*C*O), 199.9 (d, ^2J(P,C) = 22.6 Hz, *trans*-*C*O); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 20.9 (s, *P*Ph_3), 81.6 (s, ^1J(W,P) = 253.1 Hz); UV/vis (CH_3CN) λ (log ϵ) = 218 (4.96), 226 (4.99), 248 (4.68), 260 (4.50), 270 (4.28), 276 (4.16), 324 (3.87), 340 (3.87), 360 (3.76); IR (KBr) $\tilde{\nu}$ 2071 (s, CO), 1962 (s, CO), 1935 (vs, CO), 1913 (vs, CO), 1742 (s, CO_2), 1722 (s, CO_2) cm^{-1}; MS (EI, ^{184}W); *m*/*z* 876 (12) $[M]^{+\bullet}$, 848 (10) $[M - CO]^+$, 820 (28) $[M - 2CO]^+$, 792 (54) $[M - 3CO]^+$, 764 (46) $[M\text{-}4CO]^+$, 736 (100) $[M - 5CO]^+$, 262 (68) $[PPh_3]^+$, 183 (64) $[PPh_2]^+$, 77 (4) $[Ph]^+$. Anal. Calcd for $C_{36}H_{26}N_2O_9P_2W$: C, 49.34; H, 2.99; N, 3.20. Found: C, 49.23; H, 3.10; N, 3.12.

{**[4,5-Bis(dimethylamino)-2-(2-ethoxycarbonylethyl)-2*H*-1,3,2-diazaphosphole-*κP*]pentacarbonyltungsten(0)**} **(14).** To a solution of 7-phosphanorbornadiene complex **3b** (1 mmol) and copper(I) chloride (0.4 mmol), dissolved in toluene (3 mL), was added dimethyl cyanamide (3 mmol). The solution was heated at 65 °C for 60 min with slow stirring. All volatile components were removed in vacuo (ca. 0.01 mbar) and the products separated by column chromatography (SiO_2, 20 °C, 10 × 2 cm, petrol ether/diethyl ether, 1:2). Evaporation of the second fractions yielded complex **14** as pale yellow solid. Yield: 440 mg (74%); ^{1}H NMR ($CDCl_3$) δ 1.18 (t, 3H, ^2J(H,H) = 7.14 Hz, CH_3(Et)), 2.02 (ABX, 2H, CH_2), 2.35 (ABX, 2H, CH_2), 2.99 (s, 12 H, $N(CH_3)_2$), 4.03 (q, 2H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 14.1 (s, CH_3(Et)), 27.7 (s, CH_2), 32.3 (d, ^1J(P,C) = 24.4 Hz, CH_2), 40.8 (d, $N(CH_3)_2$, ^2J(P,C) = 27.5 Hz), 61.2 (s, OCH_2), 162.9 (d, ^2J(P,C) = 5.3 Hz, N−C═N), 172.3 (d, ^3J(P,C) = 10.6 Hz, CO_2), 196.6 (d, ^2J(P,C) = 8.2 Hz, *cis*-CO), 200.5 (d, ^2J(P,C) = 24.1 Hz, *trans*-CO); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 127.9 (s, ^1J(W,P) = 268.2 Hz); MS (^{184}W) *m*/*z* 597 (23) $[M]^+$, 568 (100) $[M - CO]^+$, 457 (67) $[M - 5CO]^+$. Anal. Calcd for $C_{16}H_{21}O_7PN_4W$: C, 32.23; H, 3.55. Found: C, 31.96; H, 3.38.

{**[4,5-Bis(dimethylamino)-2-(2-methyl)-2*H*-1,3,2-diazaphosphole-*κP*]pentacarbonyltungsten(0)**} **(16).** To a solution of 7-phosphanorbornadiene complex **3c** (1 mmol) and copper(I) chloride (0.4 mmol), dissolved in toluene (3 mL), was added dimethyl cyanamide (3 mmol). The solution was heated at 65 °C for 60 min with slow stirring. All volatile components were removed in vacuo (ca. 0.01 mbar) and the products separated by column chromatography (SiO_2, 20 °C, 10 × 2 cm, petrol ether/diethyl ether, 1:2). Evaporation of the second fractions yielded complex **16** as pale yellow solid. Yield: 400 mg (78%); ^{1}H NMR ($CDCl_3$) δ 1.8 (d, 3H, ^2J(P,H) = 6.8 Hz, PCH_3), 3.04 (s, 12H, $N(CH_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 25.0 (d, ^{1}J(P,C) = 26.8 Hz, PCH_3), 41.3 (s, $N(CH_3)_2$), 162.3 (d, ^2J(P,C) = 6.2 Hz, N−C═N), 197.1 (d, ^2J(P,C) = 8.5 Hz, *cis*-CO), 201.1 (d, ^2J(P,C) = 23.0 Hz, *trans*-CO); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 126.5, ^1J(W,P) = 266.0 Hz; MS (EI, ^{184}W) *m*/*z* 510 (69) $[M]^+$, 483 (41) $[M - CO]^+$, 369 (100) $[M - 5CO]^+$. Anal. Calcd for $C_{12}H_{15}O_5PN_4W$: C, 28.26; H, 2.96. Found: C, 28.31; H, 3.03.

Synthesis of Complex 16 via Reaction of 14 with the System KO*t*Bu/MeI. Complex **14** (0.2 g, 0.29 mmol) was dissolved in 4 mL of THF and cooled to 0 °C, and 0.039 g (0.0345 mmol) of KO*t*Bu was added (the addition was done four times, after 20 min each). After warming to ambient temperature (in 18 h) and additional stirring for 5 h, 1.5 mL of methyliodide was added and the solution stirred for 15 h at ambient temperature. All volatile components were removed in vacuo (ca. 0.01 mbar) and the products separated by low-temperature column chromatography (SiO_2, −10 °C, 10 × 2 cm, petrol ether/diethyl ether, 3:7). Evaporation of the second fraction yielded complex **16** as a pale yellow solid. Yield: 76 mg (51%).

X-ray Crystallographic Analyses. For crystal data and structure refinement of complexes **11a**−**d** see Table 2. The data were registered with a Bruker SMART 1000 CCD diffractometer; absorption corrections were based on SADABS. The structures were solved by the heavy atom method and refined anisotropically by full-matrix least-squares on F^2.[28] Hydrogen atoms were included using a riding model or rigid methyl groups.

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Supporting Information Available: For **11a**−**d**, tables of crystal data and structure refinement details, atomic coordinates, displacement parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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