Synthesis of 2*H*-1,2-Azaphosphole Complexes by [3 + 2] Cycloaddition of Nitrilium Phosphane−Ylide Complexes with Various Alkynes: Studies of the C-Substituent and Metal Effects on the Reaction Course

Hendrik Wilkens, Annette Ostrowski, Jörg Jeske, Frank Ruthe, Peter G. Jones, and Rainer Streubel*

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

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Thermal ring opening of [2-(bis(trimethylsilyl)methyl)-3-phenyl-2*H*-azaphosphirene-κP]-pentacarbonylchromium(0), -molybdenum(0), or -tungsten(0) (**1a**−**c**) in the presence of three different alkynes, phenylacetylene, ethyl acetylenecarboxylate (EAC), and dimethyl acetylenedicarboxylate (DMAD) (**i**−**iii**), was investigated, using toluene (**a**) and benzonitrile (**b**) as solvents, whereby special emphasis was to determine the dependence of the [2 + 1]/[3 + 2] cycloaddition product ratio and the regioselectivity on the electronic properties of the acetylenes and the transiently formed nitrilium phosphane−ylide complexes. It is shown that the stability of the latter clearly depends on the donor abilities of the C-substituent of the C,N,P 1,3-dipole system. In toluene 1*H*-phosphirene complexes **11a**−**c** are obtained exclusively (**ia**), whereas when EAC (**iia**) and DMAD (**iiia**) were employed as trapping reagents, the metal-dependent formation of either a mixture of 1*H*-phosphirene and 2*H*-1,2-azaphosphole complexes (M = Cr, W; **iia**, **12a**,**c** and **13a**,**c**; **iiia**, **4a,c** and **5c**) or a mixture of 1*H*-phosphirene and a diphosphene complex was observed (M = Mo; **iia**, **12b** and **14**; **iiia**, **4b** and **14**). Reaction **iia** yielded **13a**,**c** regioselectively. Exclusively in the case of DMAD (**iiia**,**b**), but for all 2*H*-azaphosphirene complexes **1a**−**c**, the further unidentified byproduct **15** was detected spectroscopically. In benzonitrile the reactions of complexes **1a**−**c** led generally to decreased yields of 1*H*-phosphirene complexes **11a**−**c** (**ib**) but not to 2*H*-1,2-azaphosphole complex formation in the case of **ib**. In the case of the reactions **iib** and **iiib**, significantly changed 1*H*-phosphirene/2*H*-1,2-azaphosphole complex ratios are observed in favor of the latter (complexes **13a**,**c** and **5c**). Although the regioisomeric complexes **13a**,**c** were formed predominantly, evidence was obtained spectroscopically, at least, for the other regioisomeric tungsten complex **18a**. The dependence of the 1*H*-phosphirene/2*H*-1,2-azaphosphole complex ratios on the arylnitrile concentration and the electronic influence of the *para* aryl substituent was demonstrated by an ^{31}P NMR spectroscopic study (**iv**) for the 2*H*-azaphosphirene complexes **1c** and **16a**,**b**. Further three-component reactions with 2*H*-azaphosphirene complexes, different nitriles, and DMAD (**v**), EAC (**vi**−**viii**), and phenylacetylene (**ix**) are reported. Thus, thermolysis of complex **1c** in acetonitrile or *tert*-butyl cyanide and with DMAD led to 5-alkyl-substituted 2*H*-1,2-azaphosphole complexes **17c**,**d** (**v**), and with acetonitrile and EAC the 2*H*-1,2-azaphosphole complex **13d** was obtained (**vi**). Thermolysis of 2*H*-azaphosphirene complexes **1a**−**c** in toluene with EAC as trapping reagent and dimethyl cyanamide (**vii**) or 1-piperidinonitrile (**viii**) selectively furnished 2*H*-1,2-azaphosphole complexes **13e**−**h** and **18b**−**e**, the former being the preferred regioisomers. Using the 2*H*-azaphosphirene complex **1c**, dimethyl cyanamide or 1-piperidinonitrile, and phenylacetylene (**ix**), the last as solvent *and* trapping reagent, gave complicated product mixtures. These consist each of three different types of main products, the 2*H*-1,2-azaphosphole complexes **21a**,**b** and the two acyclic, isomeric complexes **22a**,**b** and **23a**,**b**, resulting from opposite 1,3-additions of the C−H function of phenylacetylene to the 1,3-dipole system of the intermediately formed *C*-dialkylamino-substituted nitrilium phosphane−ylide complexes **10** and **19c**; reaction **ix** shows that stability *and* reactivity significantly depend on the C-substituent of the C,N,P 1,3-dipole system. The structures of the 2*H*-1,2-azaphosphole complex **21a** and of the [bis(trimethylsilyl)methyl](trimethylsiloxy)phosphane complex **24c** were determined by single-crystal X-ray diffraction.

Introduction

The chemistry of N-heterocycles such as azoles[1] and pyrazoles[2] has been studied thoroughly, and today, these systems represent classical heteroarenes and, therefore, form a part in every basic organic chemistry textbook. Extensive studies have also focused on their

* To whom correspondence should be addressed. Telefax: Int. + 531/391−5387. E-mail: r.streubel@tu-bs.de.

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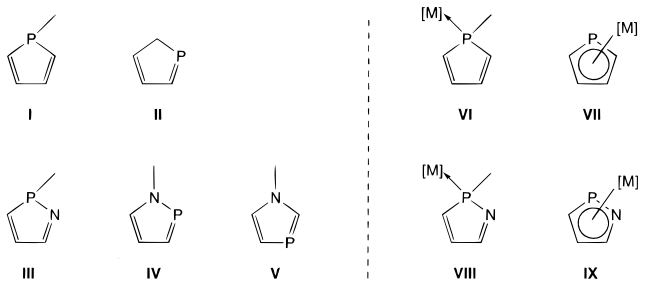
Chart 1



P-analogues, the phospholes[3] (**I** and **II**), but much less work has been done with azaphospholes[4] (**IV** and **V**) (Chart 1). One of the most interesting issues of these studies was the potential aromaticity of phospholes and azaphospholes; the 2*H*-phosphole (**II**) is not aromatic at all and behaves like other compounds having a $\sigma^2\lambda^3$-phosphorus.[5] In contrast, it was found that the azaphospholes **IV** and **V** have aromaticities similar to those of their parent N-heterocycle systems.[4] For the 1*H*-phospholes (**I**), a discussion of more than 3 decades seemed to be over, with the general acceptance that they are only weakly aromatic in most cases because of the inherent pyramidal preference[6] of $\sigma^3\lambda^3$-phosphorus in its compounds[7] and consequent nonparticipation of the phosphorus lone pair in cyclic electron delocalization. New investigations demonstrated that phospholes could gain some aromaticity[8,9] if bulky substituents were employed at the phosphorus center[10] or electron-withdrawing groups at carbon,[11] leading to a more planarized coordination environment at phosphorus, which may even become planar upon formal substitution of two CH fragments by two phosphorus atoms as in 1-[bis(trimethylsilyl)methyl]-3,5-bis(trimethylsilyl)-1,2,4-triphosphole.[12]

We became interested in this area when we synthesized the first 2*H*-1,2-azaphosphole tungsten complexes[13] (type **VIII**) having the novel 2*H*-1,2-azaphosphole **III** as ligand system, which still is unknown in the noncoordinated form.[14] Furthermore, regarding the synthetic potential of η^1-phosphole[3a] (**VI**) and η^5-phospholide complexes[15] (**IX**), we decided to exploit our synthetic route to 2*H*-1,2-azaphosphole complexes and to investigate their chemistry, which might give access to the free heterocycle and also, in the longer terms, to η^5-1,2-azaphospholide complexes of type **IX** (Scheme 1).

First and foremost we focused our interest on the investigation of [3 + 2] cycloaddition reactions of nitrilium phosphane−ylide complexes to alkynes, a reaction that was first reported for the synthesis of the 5-phenyl-substituted 2*H*-1,2-azaphosphole complex **5c**;[13] in this case the 1*H*-phosphirene complex **4c** was obtained as the main product and complex **5c** only as a byproduct (Scheme 1). In another preliminary study, we reported a three-component reaction, using the 2*H*-azaphosphirene complex **1c**, dimethyl acetylenedicarboxylate (DMAD), and dimethyl cyanamide, which led to the 5-(dimethylamino)-substituted 2*H*-1,2-azaphosphole complex **6** and the two diastereomeric Δ^3-1,3,2-oxazaphospholene complexes **7a,b**.[16] In two other related experiments we assumed as reactive intermediates, besides the terminal phosphanediyl complex **3c** (Scheme 2), nitrilium phosphane−ylide complexes **2c** and **10**, which displayed different regioselectivities toward benzonitrile; complex **2c** furnished a mixture of 2*H*-1,2,4-diazaphosphole complex **8** and 2*H*-1,3,2-diazaphosphole complex **9a**,[17] whereas complex **10** gave selectively the 2*H*-1,3,2-diazaphosphole complex **9b**[18] (Scheme 2).

Here we report detailed studies of 2*H*-1,2-azaphosphole complex formation, with special regard to the effect of (1) the metal and the C-substituent effect of transiently generated nitrilium phosphane−ylide complexes and (2) the alkyne substitution pattern on the regioselectivity of the [3 + 2] cycloaddition reactions and the reaction course in general. We further report the single-crystal X-ray structure analyses of 2*H*-1,2-azaphosphole complex **21a** and of [bis(trimethylsilyl)methyl](trimethylsiloxy)phosphane complex **24c**.

Results and Discussion

Synthesis of 5-Phenyl-2*H*-1,2-azaphosphole Complexes. A. Investigations of the Thermolysis of 2*H*-Azaphosphirene Complexes in Toluene or

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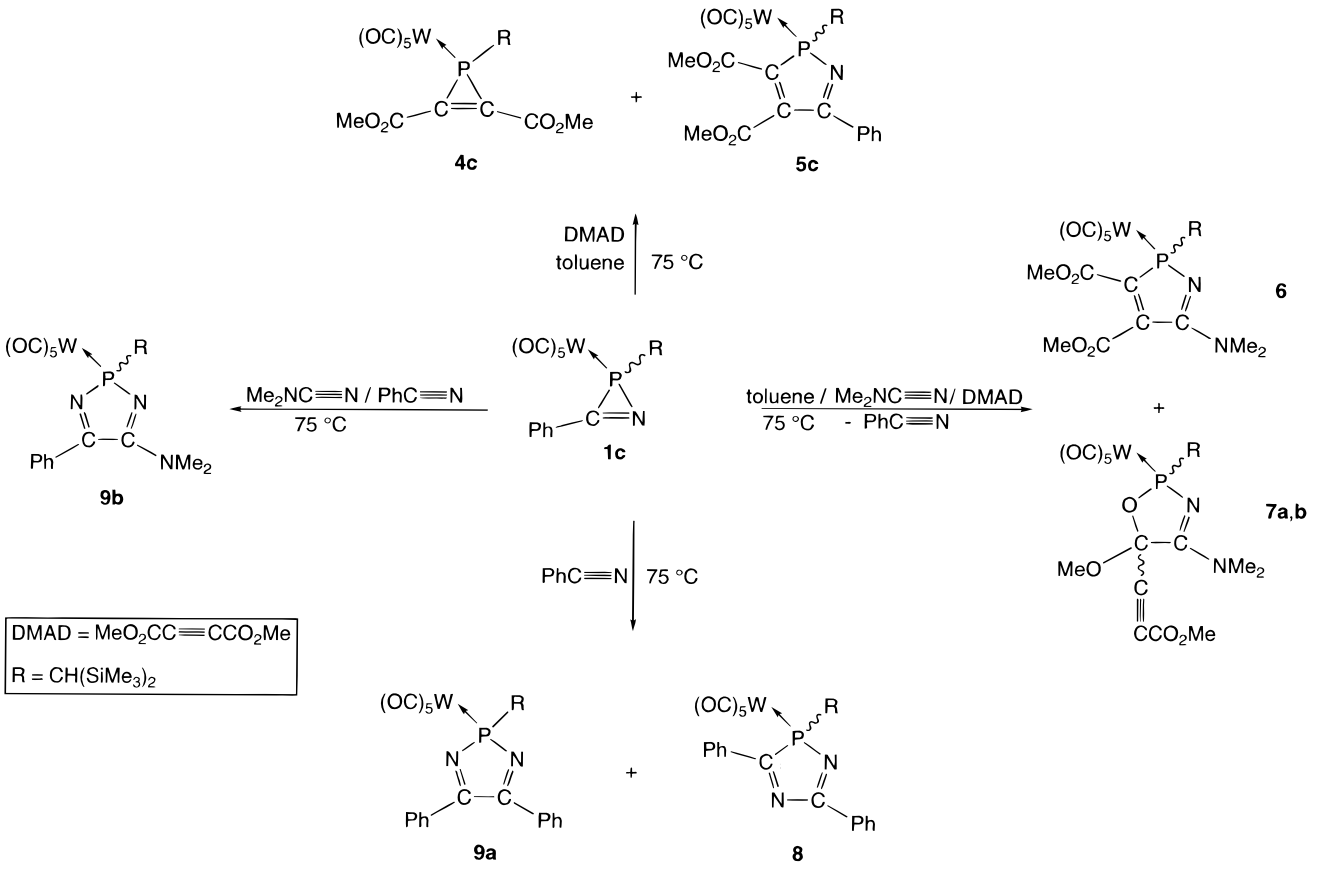
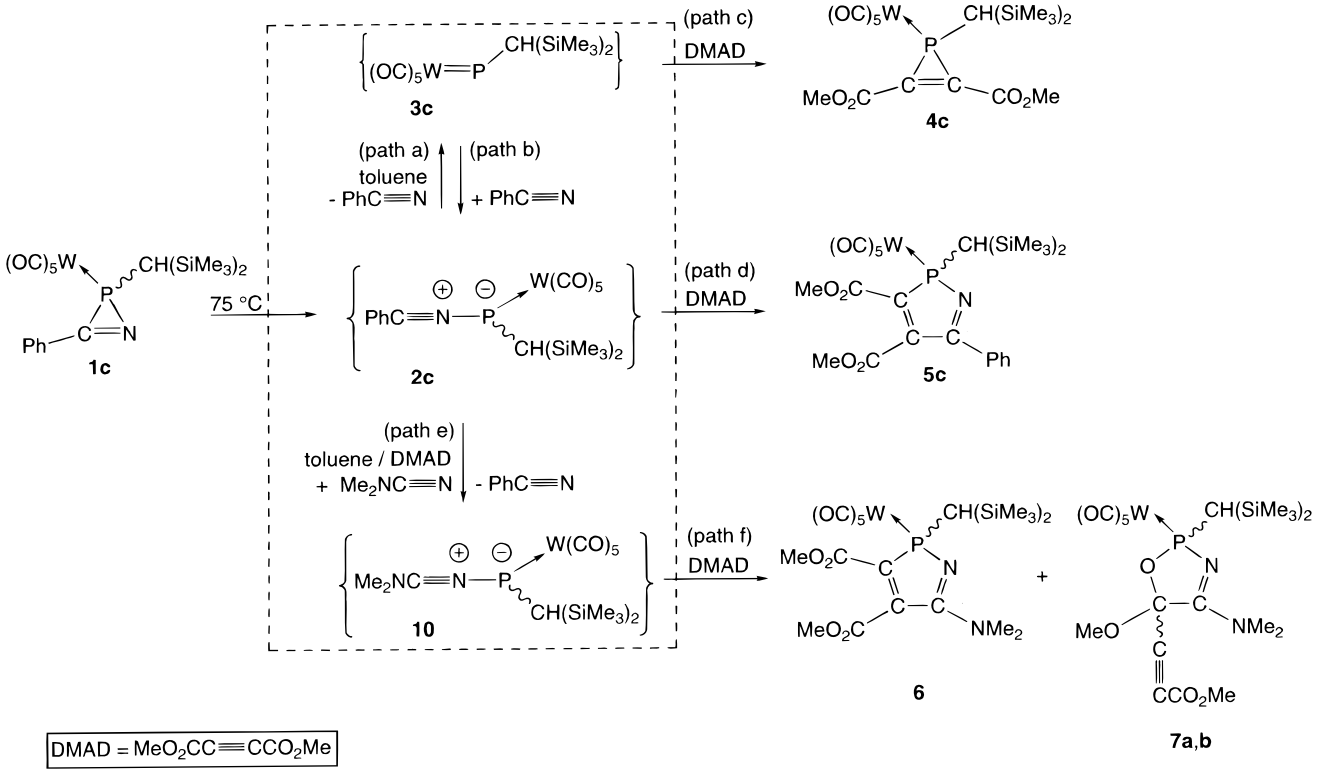
Scheme 1

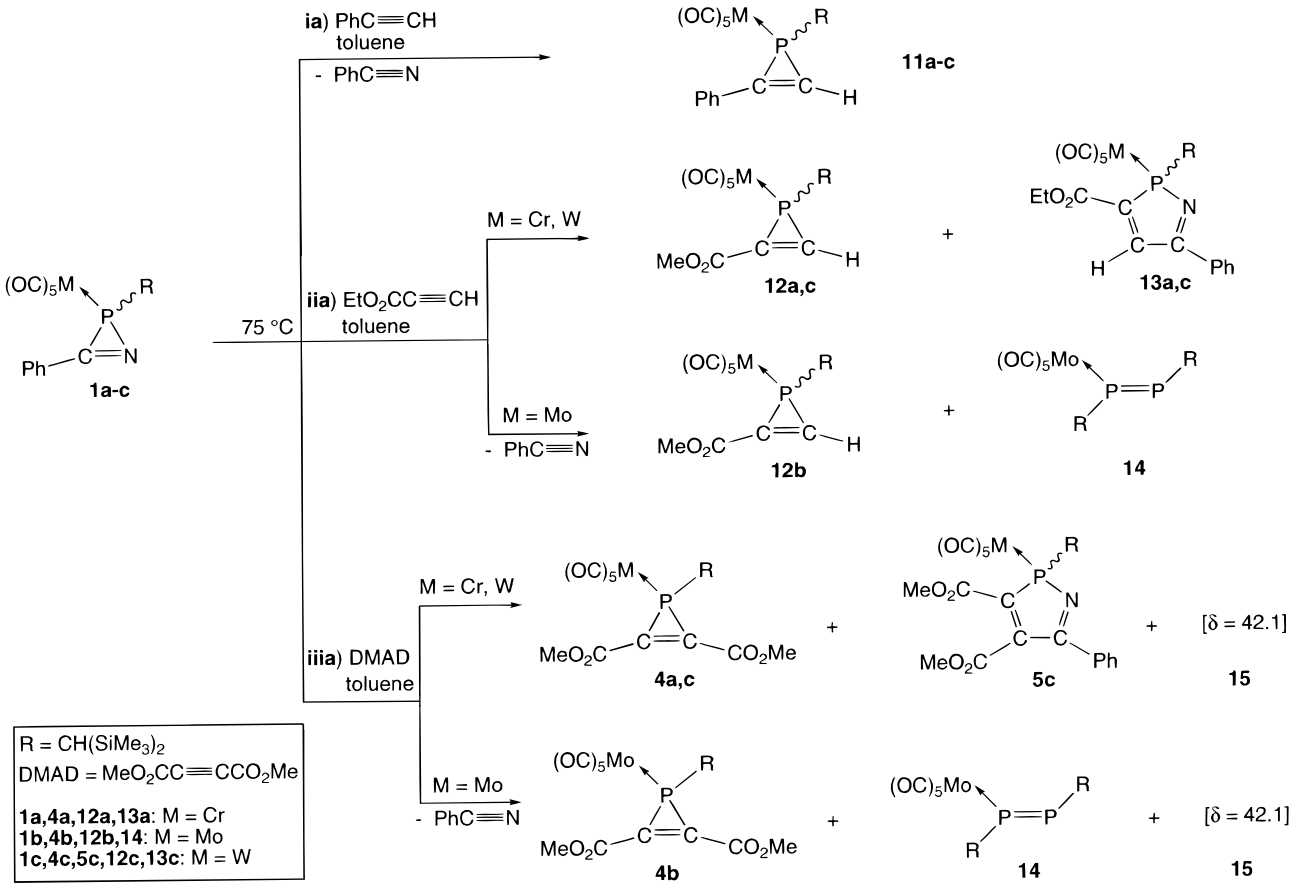


Scheme 2



Benzonitrile and in the Presence of Alkynes. Our investigations of the thermolysis of 2*H*-azaphosphirene tungsten complex **1c** in toluene had shown previously that [2 + 1] cycloaddition products, 1*H*-phosphirene complexes,[19] were obtained —with one exception[13]— if various alkynes were used as trapping reagents.[20] We were thus interested in investigating the thermolysis of the 2*H*-azaphosphirene complexes **1a**[21] and **1b**,**c**[22] in

Scheme 3



toluene or benzonitrile in the presence of various, electronically different alkynes, especially emphasizing the effect of the metal and the C-substituent of transiently generated nitrilium phosphane−ylide complexes and the alkyne substitution pattern on the reaction course.

Thermolysis of 2*H*-azaphosphirene complexes **1a**−**c** in toluene (Scheme 3) with 2 equiv of phenylacetylene (**ia**) yielded the 1*H*-phosphirene complexes **11a**,**b** and **11c**[18b] in moderate to good yield (Table 1); selected NMR data of **11a**−**c** are collected in Table 3 and will be discussed below together with those of other products mentioned hereafter. If the reaction of complexes **1a**,**c** was carried out with ethyl acetylenecarboxylate (EAC) (**iia**) or dimethyl acetylenedicarboxylate (DMAD) (**iiia**) as trapping reagents, the formation of mixtures of 1*H*-phosphirene complexes **4a**,**c** and **12a**,**c** and 2*H*-1,2-azaphosphole complexes **13a**,**c** and **5c**[13] (**iia**, **iiia**: M = Cr, W) was observed; in reaction **iia** the 3-ethylcarboxylate-substituted 2*H*-1,2-azaphosphole complexes **13a**,**c** were formed regioselectively; for NMR data of complexes **13a**,**c** see Table 4. This situation differs markedly from that found for the reaction of the 2*H*-azaphosphirene molybdenum complex **1b**; in both reactions (**iia** and **iiia**) a mixture of the 1*H*-phosphirene complexes **4b** and **12b** and the diphosphene complex **14**[23] was formed. In contrast to the former, the latter complex could be isolated, displaying, for example, the following known ^{31}P NMR data (toluene): δ 463.8 (d), 434.0 (d, ^1J(P,P) = 515.0 Hz) (cf.[23] (CD_2Cl_2) δ 465.4 (d), 433.0 (d, ^1J(P,P) = 515.0 Hz)). Noteworthy also is the finding that, in the case of DMAD, and for all 2*H*-azaphosphirene metal complexes **1a**−**c** the byproduct **15** was detected spectroscopically (Table 1) but, unfortunately, could not be isolated by low-temperature column chromatography. Nevertheless, further experiments showed that the formation of **15** depends on an intermediately formed product having a phosphorus NMR resonance at δ 85.5; this intermediate was observed throughout all thermolyses of 2*H*-azaphosphirene complexes **1a**−**c**. Therefore, we assume that decomplexation of the 2*H*-1,2-azaphosphole complexes takes place, giving the uncoordinated 2*H*-1,2-azaphosphole, which then reacts with DMAD in an unknown fashion to give product **15**.

Using benzonitrile (Table 1) as solvent for the thermolysis of 2*H*-azaphosphirene complexes **1a**−**c** and phenylacetylene (**ib**) led to significantly decreased yields of 1*H*-phosphirene complexes **11a**−**c**. This was far more pronounced for the molybdenum complex **11b**, and furthermore, the diphosphene complex **14** was formed as well. The reaction **iib** using EAC as trapping reagent

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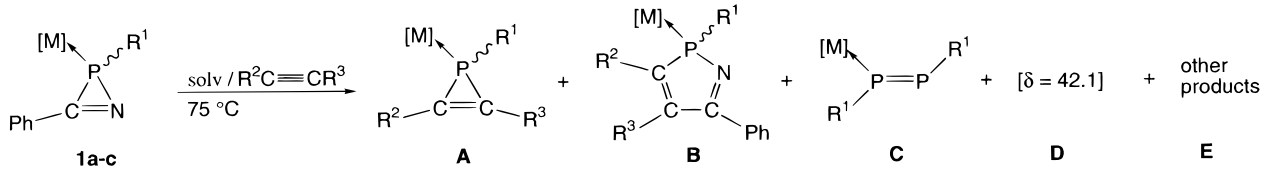
Table 1. Product Distribution[a] of the Thermolysis of Complexes 1a−c at 75 °C (1.5 h) (i−iii) Using Toluene (a) or Benzonitrile (b) as Solvents and 2 Equiv of the Trapping Reagents R^1CCR^2 (ia,b, R^1 = Ph, R^2 = H; iia,b, R^1 = Co_2Et, R^2 = H; iiia,b, R^1 = R^2 = Co_2Me) Yielding Products A−E



[M] = $M(CO)_5$; M = Cr, Mo, W; R^1 = $CH(SiMe_3)_2$

	Cr						Mo						W					
reacn	**1a**	**A**	**B**	**C**	**D**	**E**	**1b**	**A**	**B**	**C**	**D**	**E**	**1c**	**A**	**B**	**C**	**D**	**E**
ia	0	97	0	0	0	3	0	96	0	0	0	4	0	98	0	0	0	2
ib	0	85	0	0	0	15	4	32	0	24	0	40	0	84	0	0	0	16
iia	0	89	5	0	0	4	39	19	0	37	0	5	0	93	4	0	0	3
iib	0	11	79	0	0	10	36	0	0	12	0	52	0	6	87	0	0	7
iiia	0	97	0	0	3	0	45	12	0	38	5	1	0	91	9	0	0	0
iiib	0	3	0	0	96	1	9	0	0	0	57	34	0	4	27	0	52	17

[a] By ^{31}P NMR signal integration estimated yields (deviation ±2%).

Table 2. Yields[a] of 1*H*-Phosphirene Complex 4c and 5-Aryl-2*H*-1,2-azaphosphole Complexes 5c and 17a,b Depending on the Equivalents of Added Arylnitriles 4-RC_6H_4CN (cf. Scheme 4)

	4-RC_6H_4CN					
	R = CF_3		R = H		R = OMe	
amt, equiv	**4c**	**17b**	**4c**	**5c**	**4c**	**17a**
0	95	5	91	9	87	13
2	90	9	85	13	58	40
4	80	16	71	26	42	54

[a] Estimated by ^{31}P NMR signal integration (deviation ±2%).

displayed significantly changed 1*H*-phosphirene/2*H*-1,2-azaphosphole complex ratios in favor of the 2*H*-1,2-azaphosphole complexes **13a**,**c** (**iib**); predominant formation of the regioisomers **13a**,**c** was observed, and only in the case of 2*H*-azaphosphirene complex **1c** was the 2*H*-1,2-azaphosphole tungsten complex **18a** detected by ^{31}P NMR spectroscopy (ratio **13c**/**18a** 12/1), but it could not be isolated. In reaction **iiib,** using DMAD as trapping reagent, the reaction course changed even more dramatically: the 1*H*-phosphirene complexes **4a**,**c** became minor products (M = Cr, W) or even disappeared for **4b** in favor of the diphosphene complex **14** (M = Mo). Furthermore, compared to toluene, significantly increased amounts of product **15** were determined in reaction **iiib**. The amount of product **15** also clearly depended on the metal complex fragment, reaching a maximum in the case of chromium (Table 1). These changes in the reaction course, depending on the solvent, toluene or benzonitrile, mainly confirm our earlier interpretations of the decomposition of the 2*H*-azaphosphirene tungsten complex **1c** (cf. Scheme 2; hypothetical pathways are enclosed with dotted lines). One significant consequence is that the decomposition of transiently formed nitrilium phosphane−ylide complexes **2a-c** (path a) can be suppressed or, more probably, reversed by adding benzonitrile (path b), thus giving higher concentrations of these reactive intermediates compared to the terminal phosphanediyl complexes[24] **3a**−**c**, as indicated, for example, by the better yields of 2*H*-1,2-azaphosphole complex **5c** (path d) compared to 1*H*-phosphirene complex **4c** (path c). Apart from this, attention should be drawn to the unusual behavior of both reactive intermediates of molybdenum, complex **2b** and complex **3b**. The latter seems to be more stabilized and/or less reactive toward toward electron-poor alkyne derivatives.

Kinetic measurements of the thermolysis of the (2*H*-azaphosphirene)tungsten complex **1c** in toluene in the presence of phenylacetylene showed that the reaction is first order in the concentration of 2*H*-azaphosphirene tungsten complex **1c** and of phenylacetylene, at least, for the initial period of ca. 30 min (Figure 1); the deviation occurring after this period could be caused by the constant increase of the benzonitrile concentration (see also below). The result of this kinetic study is also confirmed by other experimental results obtained during reactivity studies of the (2*H*-azaphosphirene)tungsten complex **1c** toward stereochemically well-defined π-systems such as alkenes[25] and/or an imine.[26]

We were also interested in studying the effect of nitrile concentration and donor capability of *para*-substituted benzonitriles. Therefore, we performed the thermolysis of three different (3-aryl-2*H*-azaphosphirene)-tungsten complexes **1c** (Ar = Ph) and **16a,b** (**16a**, Ar = 4-$MeOC_6H_4$; **16b**, Ar = 4-$(F_3C)C_6H_4$) in toluene in the presence of DMAD and varying amounts of the three corresponding arylnitriles (**iv**) and determined the product yields by ^{31}P NMR spectroscopy, assuming similar relaxation times of the products. The result, shown in Table 2, is that the yields of 2*H*-1,2-azaphosphole complexes **5c** and **17a**,**b**[13] clearly depend on the concentrations of the appropriate nitriles and their σ-donor abilities, which are tuned by the *para* substituent.

B. Investigations on Three-Component Reactions of 2*H*-Azaphosphirene Complexes Using Dif-

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Table 3. Selected NMR Spectroscopic Data[a] of 1*H*-Phosphirene Complexes 4a−c,[20b] 11a−c,[20b] and 12a−c

	M	R^1	R^2	$\delta(^{31}P)$	$\lvert^1J(P,W)\rvert$	$\delta(^{13}C^2)$	$\lvert J(P,C^2)\rvert$	$\delta(^{13}C^3)$	$\lvert J(P,C^3)\rvert$	$\delta(^1H^{C3})$	$\lvert J(P,H^{C3}\rvert$	$\delta(^{13}CH)$	$\lvert J(P,CH)\rvert$
11a	Cr	Ph	H	−80.7		146.9	21.1	125.5	9.5	8.47	21.4	28.3	33.1
11b	Mo	Ph	H	−112.1		145.5	21.8	124.6	10.6	8.64	22.4	27.6	33.6
11c	W[20b]	Ph	H	−136.8	272.1	145.8	17.9	124.7	6.5	8.40	21.6	27.8	27.2
12a	Cr	CO_2Et	H	−53.8		141.4	20.3	143.8	14.8	9.04	21.6	28.3	29.9
12b	Mo	CO_2Et	H	−87.1[b]		*c*	*c*	*c*	*c*	*c*	*c*	*c*	*c*
12c	W	CO_2Et	H	−110.8	278.4	140.5	16.7	142.7	8.3	8.95	21.7	27.8	24.2
4a	Cr	CO_2Me	CO_2Me	−18.2		144.3	19.9	144.3	19.9			29.6	30.5
4b	Mo	CO_2Me	CO_2Me	−45.2		143.5	20.2	143.5	20.2			29.3	31.4
4c	W[20b]	CO_2Me	CO_2Me	−74.6	281.1	143.2	17.2	143.2	17.2			28.1	25.2

[a] In $CDCl_3$ unless otherwise noted. δ values are given in ppm and J values in Hz. [b] Toluene. [c] Not isolated.

Table 4. Selected NMR Spectroscopic Data[a] of 3-Ethoxycarbonyl-Substituted 2*H*-1,2-Azaphosphole Complexes 13a−h

	M	R^1	R^2	R^3	$\delta(^{31}P)$	$\lvert^1J(P,W)\rvert$	$\delta(^1H^{C4})$	$\lvert J(P,H^{C4}\rvert$	$\delta(^{13}C^3)$	$\lvert J(P,C^3)\rvert$	$\delta(^{13}C^4)$	$\lvert J(P,C^4)\rvert$	$\delta(^{13}C^5)$	$\lvert J(P,C^5)\rvert$
13a	Cr	CO_2Et	H	Ph	138.7		8.38	32.4	138.0	22.8	162.1	5.4	169.3	10.4
13c	W	CO_2Et	H	Ph	94.4	227.7	8.41	32.7	138.0	23.5	162.4	9.0	170.5	9.6
13d	W	CO_2Et	H	Me	90.4	227.3	8.53	32.4	136.8	25.8	164.3	9.2	172.8	12.0
13e	W	CO_2Et	H	NMe_2	78.1	239.2	8.13	28.7	134.6	17.7	162.1	5.0	162.3	2.5
13f	Cr	CO_2Et	H	pip	121.6		8.25	28.6	134.9	17.4	162.0	1.6	161.0	3.8
13 g	Mo	CO_2Et	H	pip	99.8		8.25	29.2	134.5	18.3	162.6	#	161.7	3.7
13h	W	CO_2Et	H	pip	77.7	239.0	8.17	28.9	134.9	18.2	162.5	5.4	161.9	2.6

[a] In $CDCl_3$. δ values are given in ppm and J values in Hz. pip = 1-piperidino. [b] Not resolved.

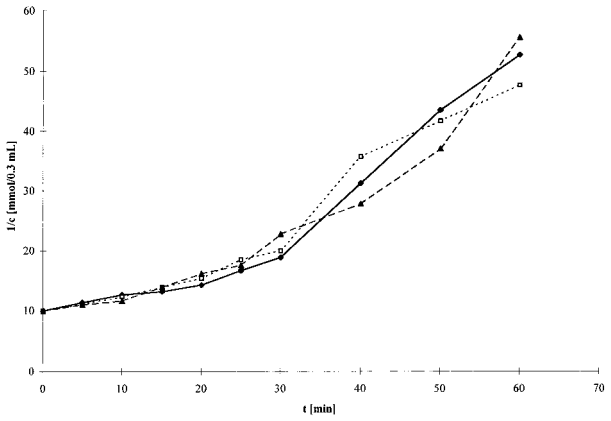


Figure 1. 1/*c* vs *t* plot of the thermolysis of complex **1c** in toluene with phenylacetylene as trapping reagent: (triangles, dashed line) phenylacetylene:**1c** = 5:1; (black squares, solid line) phenylacetylene:**1c** = 2:1; (white squares, dotted line) phenylacetylene:**1c** = 1:1.

ferently Substituted Nitriles and Alkynes Furnishing 2*H*-1,2-Azaphosphole Complexes. To examine more closely the above-mentioned assumption of suppression versus reversion of the decomposition of transiently formed nitrilium phosphane−ylide complexes **2a**−**c** (cf. Scheme 2), we thermolyzed the 2*H*-azaphosphirene tungsten complex **1c** in different alkyl cyanides, acetonitrile, and *tert*-butyl cyanide and in the presence of DMAD. These nitriles should mimic the solvent effect of benzonitrile but should give rise to 5-alkyl-substituted 2*H*-1,2-azaphosphole complexes by reaction of new transiently formed *C*-alkyl-substituted nitrilium phosphane−ylide complexes with DMAD, if the reversion pathway (path b*)* is predominant. In doing so (Scheme 4, **v**), the reactions yielded the 1*H*-phosphirene complex **4c** and the 5-alkyl-substituted 2*H*-1,2-azaphosphole complexes **17c**,**d** (**4c**:**17c** = 74:21 and **4c**:**17d** = 75:20 according to ^{31}P NMR spectroscopy); in the case of *tert*-butyl cyanide another byproduct was formed with a resonance at 280.6 ppm, which could not be further characterized. For NMR data of the 2*H*-1,2-azaphosphole complexes **17c**,**d** see Table 6. The low yield of complex **17d** points to a decreased stability under the condition of column chromatography. These results of reaction **v** clearly demonstrate that reaction of terminal phosphanediyl complex **3c** with the alkyl cyanides generated the corresponding *C*-alkyl nitrilium phosphane−ylide complexes, and in conclusion, a reversion of the decomposition in the case of benzonitrile has to be assumed (cf. Scheme 2, path b).

These findings raised our confidence in the successful use of acetonitrile as solvent and reaction component (see below) with EAC and the 2*H*-azaphosphirene complex **1c** for 2*H*-1,2-azaphosphole complex synthesis. Indeed, the reaction **vi** furnished the 1*H*-phosphirene complex **12c** and the 2*H*-1,2-azaphosphole complex **13d** (ratio 60:30) (Scheme 5) and although we could only separate a 1:1 mixture, the identity of complex **13d** was unambiguously confirmed by its NMR spectroscopic data (Table 4). From our preliminary study,[16] using 2*H*-azaphosphirene complex **1c**, 2 equiv of dimethyl cyanamide, DMAD, and toluene as solvent, we already knew two things: (1) we can formally exchange the nitrile moiety in nitrilium phosphane−ylide complex **2c** and (2) the resulting new intermediate **10** reacts with the carbon−carbon triple bond *and* the carbon−oxygen double bond of DMAD to give complexes **6** and **7a**,**b** (cf. Scheme 2), thus showing a unprecedented dual reactivity of a 1,3-dipole system toward the otherwise very frequently used trapping reagent DMAD. Furthermore, we had shown that intermediate complexes **2c** and **10** display different regioselectivities toward benzonitrile; the former gave both regioisomers, the 2*H*-1,4,2-diazaphosphole complex **8** (predominantly) and 2*H*-1,3,2-diazaphosphole complex **9a**,[17] and the latter exclusively the 2*H*-1,3,2-diazaphosphole complex **9b**.[18] Therefore, our new study had two main aims: (1) examining the metal and the C-dialkylamino substituent effect of transiently generated nitrilium phosphane−ylide complexes on the regioselectivity and (2) the π-system selectivity toward EAC compared to *C*-phenyl-substituted intermediates **2a**,**c**. We first performed a three-component reaction in toluene with the 2*H*-azaphos-

Scheme 4

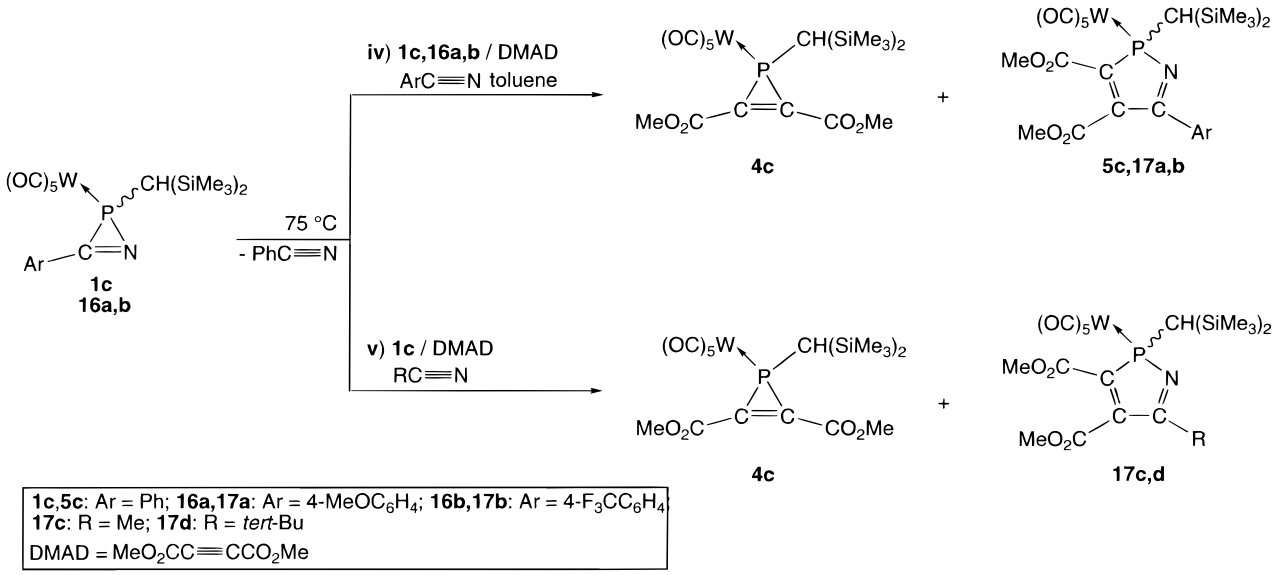


Table 5. Selected NMR Spectroscopic Data[a] of 4-Substituted 2*H*-1,2-Azaphosphole Complexes 18a−e and 21a,b and Phosphole Complex 25[28]

	M	R^1	R^2	R^3	$\delta(^{31}P)$	$\lvert^1J(P,W)\rvert$	$\delta(^1H^{C3})$	$\lvert J(P,H^{C3})\rvert$	$\delta(^{13}C^3)$	$\lvert J(P,C^3)\rvert$	$\delta(^{13}C^4)$	$\lvert J(P,C^4)\rvert$	$\delta(^{13}C^5)$	$\lvert J(P,C^5)\rvert$
18a	W	H	CO_2Et	Ph	102.8	237.4	*b*	*b*	*b*	*b*	*b*	*b*	*b*	*b*
18b	W	H	CO_2Et	NMe_2	87.6	248.9	*b*	*b*	*b*	*b*	*b*	*b*	*b*	*b*
18c	Cr	H	CO_2Et	pip	131.7		*b*	24.0	*b*	*b*	*b*	*b*	*b*	*b*
18d	Mo	H	CO_2Et	pip	108.0		*b*	*c*	*b*	*b*	*b*	*b*	*b*	*b*
18e	W	H	CO_2Et	pip	86.2	248.7	7.53	27.1	133.8	20.1	163.4	3.7	161.0	3.1
21a	W	H	Ph	NMe_2	73.1	236.8	7.60	30.9	156.0	11.7	144.7	16.5	165.6	*d*
21b	W	H	Ph	pip	73.4	236.4	7.58	31.1	155.5	12.2	145.0	16.9	165.8	1.3
25[28]	W	H	CO_2Et	Ph	21.6	217.3	7.39	33.3	138.7	32.6	146.7	12.7	145.5	7.9

[a] In $CDCl_3$. δ values are given in ppm and J values in Hz. pip = 1-piperidino. Only tentative assignments of the C4 and C5 resonances of **25** are given. [b] Not isolated. [c] Low intensity. [d] Not resolved.

Table 6. Selected NMR Spectroscopic Data[a] of 3,4-Bis(methoxycarbonyl)-Substituted 2*H*-1,2-Azaphosphole Complexes 5c, 6 and 17c,d

	R	$\delta(^{31}P)$	$\lvert J(P,W)\rvert$	$\delta(^{13}C^3)$	$\lvert J(P,C^3)\rvert$	$\delta(^{13}C^\beta)$	$\lvert J(P,C^\beta)\rvert$	$\delta(^{13}C^\beta)$	$\lvert J(P,C^\beta)\rvert$
5c[13]	Ph	102.8	237.9	142.7	25.9	162.7	13.1	162.0	1.4
17c	Me	104.2	238.5	139.7	27.9	163.8	2.3	163.5	*b*
17d	*t*-Bu	97.6	238.0	143.2	16.0	162.9	12.6	161.7	*b*
6[16]	Me_2N	85.6	249.7	139.2	21.2	158.4	5.3	161.8	5.3

[a] In $CDCl_3$. δ values are given in ppm and J values in Hz. [b] Not resolved.

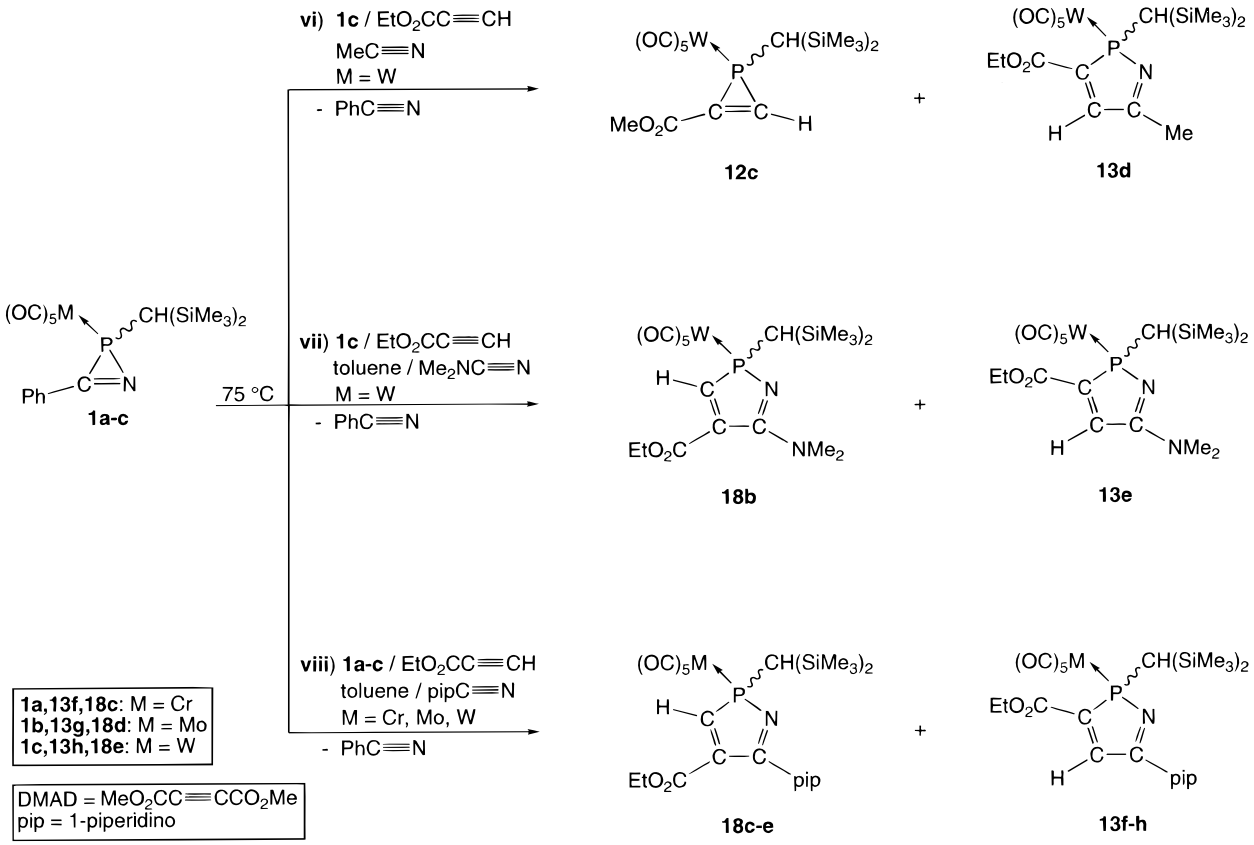
phirene complex **1c**, dimethyl cyanamide, and EAC (**vii**), to check the reactivity of transiently formed complex **10**. We observed the formation of both regioisomeric 2*H*-1,2-azaphosphole complexes **13e** and **18b** (ratio 10:1). However, because our attempts to isolate 2*H*-1,2-azaphosphole complex **18b** failed and we already knew[17] that the 1-piperidino substituent furnishes three- and five-membered heterocycle complexes that are more stable than *C*-dimethylamino-substituted systems, we employed the bulkier 1-piperidinonitrile in three-component reactions with 2*H*-azaphosphirene complexes **1a**−**c** and EAC (**viii**) (Scheme 5).

Once again, both regiosisomers of the 2*H*-1,2-azaphosphole complexes were formed in reaction **viii** and, in contrast to the situation of reaction **vii**, complexes **13f**−**h** *and* complex **18e** could be isolated (complexes **18c**,**d** were detected only by ^{31}P NMR spectroscopy); for selected NMR data of **13e**,**f** see Table 4, and for **18a**−**e** see Table 5. The 3-ethoxycarbonyl- (major isomer) and 4-ethoxycarbonyl-substituted (minor isomer) 2*H*-1,2-azaphosphole complex ratios depended also on the metal (**13a**:**18a** = 71:9, **13b**:**18b** = 71:6, **13c**:**18c** = 73:17). Concerning the regioselectivity, we were surprised about the outcome of the reactions **vii** and **viii**, because we had expected to observe a greater difference in regioselectivity of complex **10** and its 1-piperidino derivatives **19a**−**c** toward EAC compared to the nitrilium phosphane−ylide complex **2c**. Also remarkable is the absence of a dual reactivity of C-dialkylamino-substituted nitrilium phosphane−ylide complexes toward the two different π-systems of EAC. This observation will be discussed further, together with our current studies on the reactivity of nitrilium phosphane−ylide complexes toward carbonyl compounds, soon.[27]

We were also interested in checking the possibility of generating transient nitrilium phosphane−ylide complexes in three-component reactions under inert solvent-free conditions, in other words using the trapping reagent, the alkyne, as solvent. Therefore, we carried

(27) Streubel, R.; Wilkens, H.; Ruthe, F.; Jones, P. G. To be submitted for publication.

Scheme 5



out another preliminary study on two three-component reactions using 2*H*-azaphosphirene complex **1c**, dimethyl cyanamide, or 1-piperidinonitrile and phenylacetylene (**ix**). These reactions gave the 1*H*-phosphirene complex **11c** only in trace yield (1−5%) and three different types of main products, the 2*H*-1,2-azaphosphole complexes **21a**,**b** (40−50%) and two acyclic compounds **22a**,**b** (15−20%) and **23a**,**b** (15−20%), whereby only the *N*-piperidino-substituted derivative **23b** could be isolated and **22b** was obtained as a 1:1 mixture with the 2*H*-1,2-azaphosphole complex **21b**. The isomeric complexes **22** and **23** probably resulted from two different 1,3-additions of the C−H function of phenylacetylene to the 1,3-dipole system of complexes **10** and **19c**; the assumed reaction course involving the intermediately formed C-dialkylamino-substituted nitrilium phosphane−ylide complexes **10** and **19c** is shown in Scheme 6. Related 1,3-addition reactions have been reported previously for nitrile ylides with terminal alkynes.[28] The fact that the 5-phenyl-substitued 2*H*-1,2-azaphosphole complex **20** could not be detected is also noteworthy. To prove the proposed reaction pathway, we performed additionally a control reaction with pure 1*H*-phosphirene complex **11c** and the dialkylamino cyanides using toluene as solvent, but no transformation of complex **11c** into the aforementioned products **21**−**23** was observed by ^{31}P NMR spectroscopy.

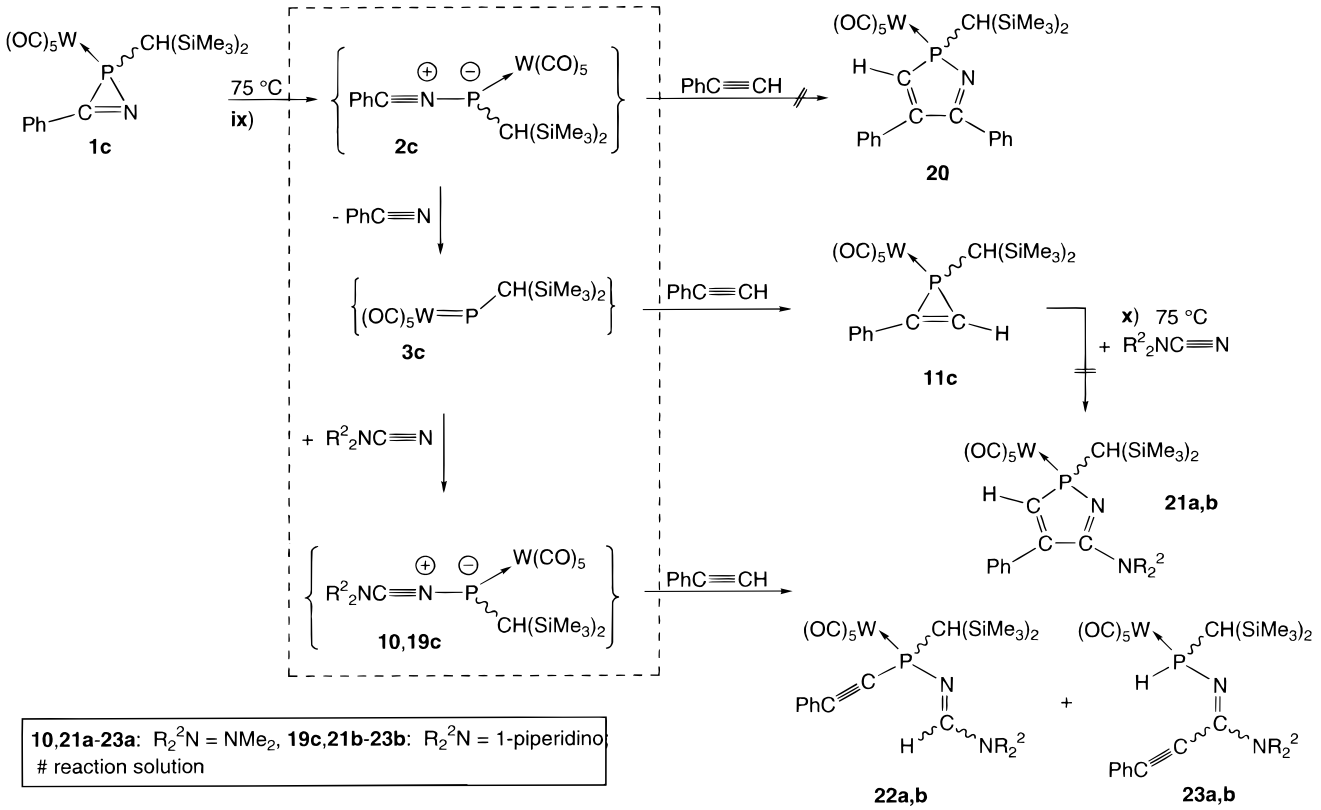
One more finding of this study deserves mention. In all reactions of 2*H*-azaphosphirene complex **1c** [$(OC)_5W$-{P(H)($OSiMe_3$)($CH(SiMe_3)_2$)}] (**24c**) was formed as a byproduct, more or less, via an unknown reaction pathway; the other complex derivatives **24a**,**b** (M = Cr, Mo) could be neither identified nor isolated. Depending on the dryness of all the reaction partners, the apparatus, the toluene and, especially, the employed nitriles, the amounts of complex **24c** varied (1−10%), but only traces of complex **24c** were formed if moisture was kept low.

(28) (a) Burger, K.; Roth, W.-D.; Neumayr, K. *Chem. Ber.* **1974**, *109*, 1984. (b) Dietlicker, K.; Heimgartner, H. *Helv. Chim. Acta* **1983**, *66*, 263.

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 herein, which had been separated and purified by column chromatography at low temperature and subsequent crystallization in most cases. NMR data will be discussed hereafter; for further analytical data see the Experimental Section. Comparison of the NMR spectroscopic data of the 1*H*-phosphirene complexes **4**, **11,** and **12** reveals some noteworthy details[19] (Table 3). The high-field phosphorus resonances of complexes **4**, **11,** and **12** display a significant dependence not only from the metal ($\Delta\delta$ = 24−33 between homologues) but also from the substituents at the C2 and C3 ring carbon atoms. Electron-withdrawing groups especially increase the magnitude of the phosphorus−tungsten coupling (272.1 Hz (**11c**), 278.4 Hz (**12c**), 281.1 Hz (**4c**)). The carbon resonances are much less affected by the substitution pattern; although C3, generally appearing at higher field due to the directly bonded hydrogen, becomes strongly deshielded in **12**, which might be caused by the β-position of this carbon in the α,β-unsaturated system. In comparison to hydrogen, electron-

Scheme 6



withdrawing groups at C2 and/or C3 lead to generally increased phosphorus−carbon coupling constants ($|J(P,C^2)| = 17-22$ Hz versus ($|J(P,C^3)| = 6-15$ Hz). All coupling constants of phosphorus to directly bonded carbon differ significantly due to the metal, whereby chromium and molydenum complexes display similar values, which are generally higher than those of tungsten complexes. The resonances for the hydrogens bonded to C3 are observed at low field (8.4−8.7 ppm (**11**) and 8.9−9.1 ppm (**12**)), having almost constant values for the phosphorus−hydrogen couplings ($|J(P,H)| = 21.4-22.4$ Hz).

Examination of the main NMR spectroscopic features of the 2*H*-1,2-azaphosphole complexes (Tables 4−6) reveals for the 3-, 4-, and 3,4-substituted derivatives ^{31}P NMR resonances in the range of 70−105 ppm for the tungsten complexes (the chromium and molybdenum complexes resonate generally at lower field), with phosphorus−tungsten coupling constants $|J(W,P)|$ of about 237−250 Hz, whereby C4-ethylcarbonyl- and C5-dialkylamino-substituted complexes tend to have relatively high values.

The assignment of the resonances to the carbon atoms of the heterocyclic system in complexes **13**, **18**, and **21** is obvious, if the carbon atoms are bonded either to phosphorus or to hydrogen leading in the first case to significantly greater magnitudes of $|J(P,C)|$ (in general) and/or to characteristic spectra, if DEPT experiments were performed. Furthermore, because of the unambiguously established structure of complex **21a** (for X-ray structure analysis see next section), we assign the resonances in the range of 161−165 ppm having small $|J(P,C)|$ values to the C5 atom of the five-membered-ring system; C4 and C5 will be both denoted as C^{β} in Table 6 (the β-notation refers to phosphorus), because in this case an unambiguous assignment was impossible. Noteworthy is the finding that the $|J(P,H^{C4})|$ values showed no significant difference for the regioisomeric complexes **13** and **18**, which is in contrast to the chemical shift values of these hydrogens. For the 3-ethoxycarbonyl-substituted 2*H*-1,2-azaphosphole complexes **13a**−**h** these resonances were observed in the range of 8.1−8.5 ppm, whereas for the 4-ethoxycarbonyl- or 4-phenyl-substituted 2*H*-1,2-azaphosphole complexes **18e** and **21a**,**b**, respectively, these were found to be between 7.5 and 7.6 ppm. A similar situation was observed for the ^{1}H NMR spectroscopic data of 4-ethoxycarbonyl-substituted phosphole complex **25**[29] having a resonance at 7.39 and a phosphorus−proton coupling of 33.3 Hz (Figure 2 and Table 5). Comparison of some ^{13}C and ^{31}P NMR spectroscopic data of phosphole complex **25** with those of 2*H*-1,2-azaphosphole complexes **18e** reveals markedly increased phosphorus−carbon couplings for the C3 atom ($|J(P,C)| = 32.6$ Hz (**25**) vs 20.1 Hz (**18e**)) and a significantly decreased phosphorus−tungsten coupling for complex **25** ($|J(P,W)| = 217.3$ Hz (**25**) vs 248.7 Hz (**18e**) or 237.4 Hz (**18a**)).

Remarkable also is the fact that the ^{31}P NMR data of complexes **5c** and **6** closely resemble those of complexes **18a**,**b**, thus showing a dominant influence of the C4- over the C3-substituent on NMR parameters of the five-membered ring.

The structures of the acyclic isomeric complexes **22a**,**b** and **23a**,**b** have been deduced from NMR and IR spectroscopic data; the configuration at the imino π-system could not be determined, thus far. The PH-functionalized phosphane complex **23b** is undoubtedly

(29) Espinosa Ferao, A.; Deshamps, B.; Mathey, F. *Bull. Soc. Chim. Fr.* **1993**, *130*, 695.

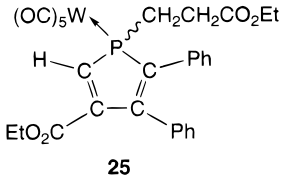


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Figure 2.

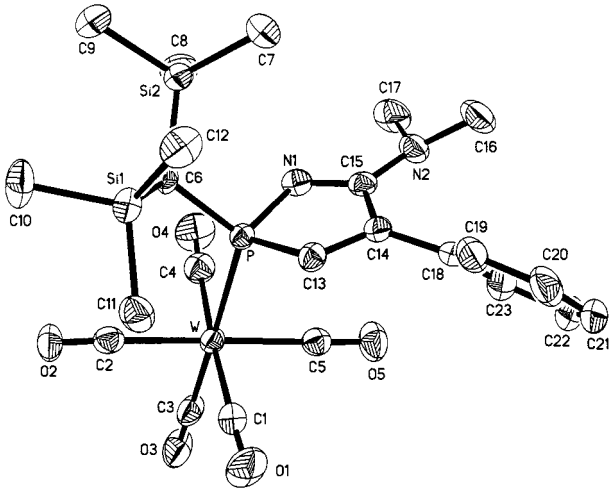

Figure 3. Molecular structure of **21a** (ellipsoids represent 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): P−N(1) = 1.690(3), N(1)−C(15) = 1.303(6), C(15)−C(14) = 1.498(6), C(14)−C(13) = 1.347(5), P−C(6) = 1.816(4), P−W = 2.5123(10), W−C(3) = 1.994(4), W−C(4) = 2.061(5), N(3)−C(15) = 1.360(5); W−P−C(6) = 118.56(13), N(1)−P−C(13) = 93.72(18), P−C(13)−C(14) = 108.3(3), C(13)−C(14)−C(15) = 110.0(4), C(14)−C(15)−N(1) = 117.0(3), C(15)−N(1)−P = 109.9(3).

characterized by its phosphorus resonance at δ 16.7 (^1J(P,W) = 249.2 Hz), the proton resonance at δ 7.93 (^1J(P,H) = 311.4 Hz and ^3J(H,H) = 1.6 Hz), the carbon resonance of the imino group at δ 143.6 (^2J(P,C) = 8.2 Hz), and the ν(C≡C) (2212 cm^{-1}) and ν(C=N) absorptions (1551 cm^{-1}) in the infrared spectrum. The isomeric complex **22b** displays, besides that for phosphorus, also typical NMR and IR data for the imino group (δ(^{1}H) 7.66 (^2J(P,H) = 29.0 Hz); δ(^{13}C) 153.7 (^2J(P,C) = 1.6 Hz)) and the ν(C=N) absorption (1604 cm^{-1}). The acetylenic carbon resonances of complex **22b** were observed at δ 89.8 7 (d, ^1J(P,C) = 33.9 Hz, *C*−P) and at δ 110.3 (d, ^2J(P,C) = 1.8 Hz, *C*C−P). Furthermore, the ν(C≡C) absorption was observed at 2163 cm^{-1} in the infrared spectrum.

Discussion of Selected X-ray Structural Data

The molecular structures of the 2*H*-1,2-azaphosphole complex **21a** and the complex **22c** were confirmed for the solid state by X-ray crystallography (Figures 3 and 4). Comparison of the most interesting structural features of the complexes **21a** and **6**[28] reveals that both complexes have almost planar five-membered-ring systems with mean deviations of 0.064 (**21a**) and 0.036 (**6**) Å. The dimethylamino groups subtend interplanar angles to the five-membered rings of 26° (**21a**) and 11.4° (**6**). Apart from localized endocyclic nitrogen−carbon and carbon−carbon double bond distances (**21a**, 1.303(6) and 1.347(5) Å; **6**, 1.312(5) and 1.338(6) Å), the rings have

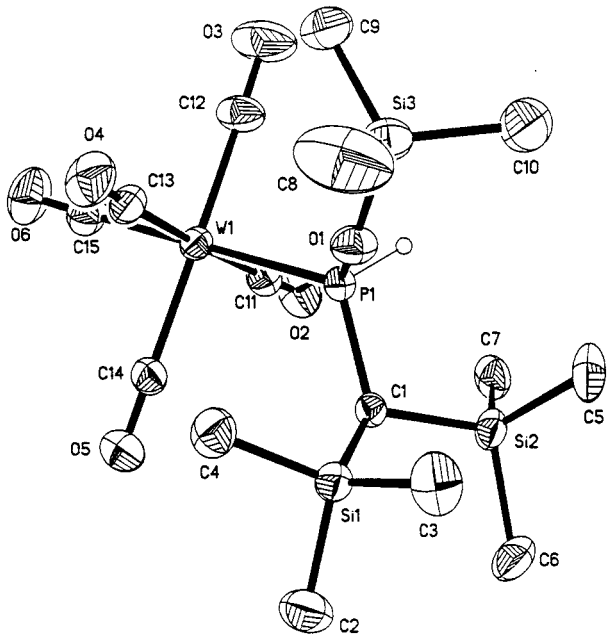

Figure 4. Molecular structure of **24c** (ellipsoids represent 50% probability level; hydrogen atoms, except P−H, are omitted for clarity). Selected bond lengths (Å) and angles (deg): P(1)−C(1) = 1.813(4), P(1)−O(1) = 1.605(3), Si(3)−O(1) = 1.661(3), Si(2)−C(1) = 1.898(4), P(1)−W(1) = 2.4822(13), W(1)−C(15) = 2.019(5), W(1)−C(13) = 2.045(5); W(1)−P(1)−C(1) = 117.31(14), W(1)−P(1)−O(1) = 118.50(13), O(1)−P(1)−C(1) = 103.75(18), P(1)−O(1)−Si(3) = 141.7(2).

also substantially shortened exocyclic nitrogen−carbon bond distances (**21a**, 1.360(5) Å; **6**, 1.346(5) Å) (cf. ref 30). Together with the angle sum at the N(2) nitrogen atom (**21a**, 354°; **6**, 360°), this provides evidence for p_π−p_π electron interactions of the nitrogen lone pair and the C−N π-bond in both complexes, which, according to these data, seems to be stronger in the case of complex **6**. Noteworthy is that this also affects the W−P distance, which is 2.5123(10) Å in complex **21a** and 2.5237(11) Å in complex **6**; the $\sum(P_{PR_3})$ values are 312.7° in complex **21a** and 310.7° in complex **6**. For **21a** the phenyl group subtends an interplanar angle to the five-membered ring of 54.6°.

The molecular structure of the secondary *P*-trimethylsiloxy-substituted phosphane complex **24c** displays a surprising similarity of the [(OC)$_5$WPCH(SiMe$_3$)$_2$] structural units of the complexes **21a** and **24c**, especially the phosphorus−carbon and phosphorus−tungsten distances and the W−P−C angles (**21a**, P−C(6) = 1.816(4) Å, P−W = 2.5123(10) Å, and W−P−C(6) = 118.56(13)°; **24c**, P(1)−C(1) = 1.813(4) Å, P(1)−W(1) = 2.4822(13) Å, and W(1)−P(1)−C(1) = 117.31(14)°). Furthermore, complex **24c** displays relatively short P(1)−O(1) and Si(3)−O(1) distances of 1.605(3) and 1.661(3) Å, respectively, and a P(1)−O(1)−Si(3) angle of 141.7(2)°. Although this bond-shortening phenomenon is already documented for triorganophosphane complexes,[31] complex **24c** is a good further example. The P−H function

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Table 7. Frontier Orbital Energies (eV) of Phenylacetylene,[33] Methyl Acetylenecarboxylate,[33] and Dimethyl Acetylenedicarboxylate[34]

alkyne	E_{HOMO}	E_{LUMO}
PhC≡CH	−10.40	1.30
MeO_2CC≡CH	−11.10	0.30
MeO_2CC≡CCO_2Me	−12.19	−0.77

of **22c** forms a hydrogen bond to O3 of a neighboring molecule, with H···O = 2.41(2) Å and P−H···O = 157(3)°.

Discussion of the Reaction Courses

The product ratios of 1*H*-phosphirene and 2*H*-1,2-azaphosphole complexes depended significantly on the electronic properties of the alkynes (**i**−**iii**), phenylacetylene, ethyl acetylenecarboxylate (EAC), and dimethyl acetylenedicarboxylate (DMAD), whereby the preference for the five-membered heterocycle complexes was DMAD over EAC and phenylacetylene; the last compound gave *none*. Furthermore, we found a pronounced regioselectivity of the reactions with EAC (**iib**), thus forming the 3-substituted 2*H*-1,2-azaphosphole complexes (estimated regioisomer ratio >12:1). These findings provide strong evidence for the assumption of transiently formed *C*-phenyl-substituted nitrilium phosphane−ylide complexes as the reactive intermediates. The regioselectivity of the complexes **2a**−**c** is as expected for [3 + 2] cycloaddition reactions of 1,3-dipoles that are directed by a HOMO-dipole−LUMO-dipolarophile interaction.[32] That this interaction dominates the reactions can be deduced directly from the LUMO energies[33,34] of these alkyne derivatives (Table 7). Therefore, the favored cycloaddition product is that formed by union of the atoms with the largest coefficient of the dipole HOMO and the dipolarophile LUMO, as established for nitrile ylides[35] and nitrile sulfides.[36]

Furthermore, the product ratios of 1*H*-phosphirene and 2*H*-1,2-azaphosphole complexes of the three-component reactions significantly depend on the Lewis-base properties of the nitrile derivatives. Strong Lewis bases such as the electron-rich dialkylamino cyanides led to the exclusive formation of the corresponding [3 + 2] cycloaddition products, thus showing a higher stability and enhanced 1,3-dipolar reactivity of the C-dialkylamino-substituted nitrilium phosphane−ylide complexes **10** and **19a**−**c.** The latter aspect is impressively demonstrated by the [3 + 2] cycloaddition reaction with phenylacetylene, which is a poor dipolarophile due to its higher LUMO energy (Table 7). The following qualitative sequence of relative stabilities and reactivities of nitrilium phosphane−ylide complexes can be deduced from the observations: 4-(trifluoromethyl)-benzonitrile < alkylnitrile < benzonitrile < 4-methoxybenzonitrile < dialkylaminonitriles.

Another interesting aspect is that the regioselectivity of *C*-phenyl- and C-alkyl-substituted nitrilium phosphane−ylide complexes toward the alkyne derivative EAC is markedly different from those of C-dialkylamino-substituted nitrilium phosphane−ylide complexes **10** and **19a**−**c** as observed in the three-component reactions (**vi**−**viii**). This C-substituent-dependent difference in regioselectivity, which is especially strong for the 1-piperidino substituent, confirms results obtained in our recent study of the reaction of complexes **2c**, **10**, and **19c** with nitriles.[17] Furthermore, there is a strong resemblance in regioselectivity between *C*-phenyl- and C-alkyl-substituted nitrilium phosphane−ylide complexes and nitrile sulfides on one hand and of C-dialkylamino-substituted nitrilium phosphane−ylide complexes and nitrile ylides on the other. Another noteworthy finding is that there is also an effect of the metal on the regioselectivity, which seems to be stronger for tungsten than for chromium or molybdenum; an observation which, for better understanding, deserves more intensive experimental and theoretical studies.

Besides the already mentioned[17] ease of N−P bond making and breaking of transiently formed nitrilium phosphane−ylide complexes, thus facilitating synthetically interesting transylidation processes, it should be noted that there is also a metal effect on the tendency of the electrophilic terminal phosphanediylmetal complexes **3a**−**c** to react with benzonitrile and on the stability of the 1,3-dipole complexes **2a**−**c** thus formed. Considering the most recent results of ab initio and DFT studies[37,38] on such phosphanediyl (phosphinidene) metal complexes of the formula $[(OC)_5MPR]$ confirms the following, widely accepted M−P bonding situation. So far, all calculated species have a singlet ground state and the major bonding contribution arises from the P→M charge transfer, but there is also π-back-bonding of the metal fragment to the phosphorus center depending mostly on the nature of the group R; the latter bonding effect is significant for PH, PCH_3, and $PSiH_3$.[38] The amount of π-back-bonding for the PH derivatives of the chromium triad has been estimated for *all* metals at ca. 41−43 kcal/mol (σ-bonding at ca. 60 kcal/mol; the corresponding PCH_3 metal complexes were not included in that study).[37] Regarding the results of our present study, which revealed an extraordinary behavior of the terminal phosphanediyl molybdenum complex **2b**, the extent of metal-to-ligand π-back-bonding in such metal complexes seems to be an unanswered question, at least for P-alkyl derivatives.

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. Solvents were dried according to standard procedures. NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz for ^1H; 50.3 MHz for ^{13}C; 81.0 MHz for ^{31}P) using [D]chloroform and [D_6]benzene as solvent and

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internal standard; shifts are given relative to external tetramethylsilane (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). Mass spectra were recorded on a Finigan MAT 8430 (70 eV); apart from *m*/*z* values of the molecule ions, only *m*/*z* values having intensities of more than 20% are given. Infrared spectra were recorded on a Biorad FT-IR 165 (selected data given). Melting points were obtained on a Büchi 535 capillary apparatus. Elemental analyses were performed using a Carlo Erba analytical gas chromatograph. All products were separated by column chromatography at low temperature. The *κP* notation in the nomenclature is intended to differentiate between P- and N-coordination of the appropriate heterocycle to the metal.

The following complexes were synthesized according to the quoted references: pentacarbonyl[2-(bis(trimethylsilyl)methyl)-3-phenyl-2*H*-azaphosphirene-*κP*]chromium(0), -molybdenum(0), and -tungsten(0) (**1a**−**c**),[22] pentacarbonyl[1-(bis(trimethylsilyl)-methyl)-2,3-bis(methoxycarbonyl)-1*H*-phosphirene-*κP*]tungsten(0) (**4c**),[20] pentacarbonyl[1-(bis(trimethylsilyl)methyl)-2-phenyl-1*H*-phosphirene-*κP*]tungsten(0) (**11c**),[20b] pentacarbonyl[2-(bis(trimethylsilyl)methyl)-3,4-bis(methoxycarbonyl)-5-phenyl-2*H*-1,2-azaphosphole-*κP*]tungsten(0) (**5c**),[13] pentacarbonyl[2-(bis(trimethylsilyl)methyl)-3,4-bis(methoxycarbonyl)-5-(4-methoxyphenyl)-2*H*-1,2-azaphosphole-*κP*]tungsten(0) (**17a**),[13] and pentacarbonyl[2-(bis(trimethylsilyl)methyl)-3,4-bis(methoxycarbonyl)-5-(4-(trifluoromethyl)phenyl-2*H*-1,2-azaphosphole-*κP*]tungsten(0) (**17b**).[13]

General Procedure for the Synthesis of (2-Phenyl-1*H*-phosphirene)metal Complexes 11a,b. Solutions of 1 mmol of 2*H*-azaphosphirene complexes **1a**,**b** in 3.0 mL of toluene and 0.25 mL of phenylacetylene (2 mmol) were heated at 75 °C for 1−2.5 h with slow stirring. Afterward, the solvent and the trapping reagent were removed in vacuo and the complexes **11a**,**b** separated by low-temperature chromatography of the residues (SiO_2, 10 × 2 cm, −20 °C, *n*-hexane/diethyl ether 97.5:2.5) and recrystallized from *n*-pentane at −20 °C.

Pentacarbonyl[1-(bis(trimethylsilyl)methyl)-2-phenyl-1*H*-phosphirene-*κP*)chromium(0) (11a). Conditions: 0.49 g of **1a**, 75 °C, 1 h. **11a**: pale yellow solid; mp 84 °C dec; yield 0.44 g (90%). ^{1}H NMR ($CDCl_3$): *δ* 0.08 (s, 9 H, $SiMe_3$), 0.26 (s, 9 H, $SiMe_3$), 0.47 (d, ^2J(P,H) = 1.5 Hz, 1 H, C*H*($SiMe_3$)$_2$), 7.49 (m_c, 3 H, Ph), 7.72 (m_c, 2 H, Ph), 8.47 (d, ^2J(P,H) = 21.4 Hz, PC*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): *δ* 1.6 (d, ^3J(P,C) = 3.1 Hz, $SiMe_3$), 1.9 (d, ^3J(P,C) = 3.4 Hz, $SiMe_3$), 28.3 (d, ^1J(P,C) = 33.1 Hz, *C*H($SiMe_3$)$_2$), 125.5 (d, $^{(1+2)}J$(P,C) = 9.5 Hz, *P*(*H*)*C*), 128.2 (d, ^2J(P,C) = 6.6 Hz, *i*-Ph), 129.1 (s, *m*-Ph), 129.3 (d, ^3J(P,C) = 2.0 Hz, *o*-Ph), 130.8 (s, *p*-Ph), 146.9 (d, $^{(1+2)}J$(P,C) = 21.1 Hz, P*C*), 216.6 (d, ^2J(P,C) = 16.0 Hz, *cis*-*C*O), 220.7 (d, ^2J(P,C) = 6.4 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): *δ* −80.7 (s). MS (70 eV, EI; ^{52}Cr); *m*/*z* (%) 484 (10) [M$^{\bullet+}$], 372 (20) [(M − 4 CO)$^+$], 344 (100) [(M − 5 CO)$^+$]. IR (KBr): *ν̃*(CO) 2060 (s), 1984 (s), 1955 (vs), 1935 (vs), 1928 (vs, br), 1924 (vs, br) cm^{-1}. Anal. Calcd for $C_{20}H_{25}O_5PSi_2Cr$ (484.6): C, 49.38; H, 5.20. Found: C, 49.76; H, 5.35.

Pentacarbonyl[1-(bis(trimethylsilyl)methyl)-2-phenyl-1*H*-phosphirene-*κP*)molybdenum(0) (11b). Conditions: 0.53 g of **1b**, 75 °C, 2.5 h. **11b**: pale yellow solid; mp 101 °C dec; yield 0.27 g (51%). ^{1}H NMR (C_6D_6): *δ* −0.02 (s, 9 H, $SiMe_3$), 0.12 (s, 9 H, $SiMe_3$), 0.38 (d, ^2J(P,H) = 2.3 Hz, 1 H, C*H*($SiMe_3$)$_2$), 7.06 (m_c, 3 H, Ph), 7.55 (m_c, 2 H, Ph), 7.64 (d, ^2J(P,H) = 22.4 Hz, PC*H*). ^{13}C{^{1}H} NMR (C_6D_6): *δ* 1.3 (d, ^3J(P,C) = 3.0 Hz, $SiMe_3$), 1.5 (d, ^3J(P,C) = 3.7 Hz, $SiMe_3$), 27.6 (d, ^1J(P,C) = 33.6 Hz, *C*H($SiMe_3$)$_2$), 124.6 (d, $^{(1+2)}J$(P,C) = 10.9 Hz, P(H)*C*), 128.7 (d, ^2J(P,C) = 6.0 Hz, *i*-Ph), 128.9 (s, *m*-Ph), 129.1 (d, ^3J(P,C) = 2.3 Hz, *o*-Ph), 130.6 (s, *p*-Ph), 145.5 (d, $^{(1+2)}J$(P,C) = 21.8 Hz, P*C*), 204.3 (d, ^2J(P,C) = 11.0 Hz, *cis*-*C*O), 207.8 (d, ^2J(P,C) = 26.3 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR (C_6D_6): *δ* −112.1 (s). MS (70 eV, EI; (^{98}Mo): *m*/*z* (%) 530 (50) [M$^{\bullet+}$], 576 (20) [(M − 2 CO)$^+$], 446 (100) [(M − 3 CO)$^+$], 400 (40) [((OC$_4$)MoPCH-($SiMe_3$)$_2$)$^+$], 73 (45) [($SiMe_3$)$^+$]. IR (KBr): *ν̃*(CO) 2072 (s), 1989 (s), 1957 (s), 1944 (s), 1908 (vs, br), 1883 (vs, sh) cm^{-1}. Anal. Calcd for $C_{20}H_{25}O_5PSi_2Mo$ (528.5): C, 45.45; H, 4.77. Found: C, 44.89; H, 4.68.

General Procedure for the Synthesis of 2-Ethoxycarbonyl-Substituted 1*H*-Phosphirene Complexes 12a,c. Solutions of 0.2/0.5 mmol 2*H*-azaphosphirene complexes **1a**,**c** in $^1/_3$ mL of toluene and 0.04/0.1 mL ethyl acetylenecarboxylate (1 mmol) were heated at 75 °C for 1/1.5 h with slow stirring. Afterward, the solvents were removed in vacuo and the products were separated by low-temperature chromatography of the residues (SiO_2, 10 × 2 cm, *n*-hexane/diethyl ether 95/5). Evaporation of the first fraction afforded **12c** as an yellow oil, and crystallization from *n*-pentane at −20 °C afforded **12c** as an orange solid.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-2-(ethoxycarbonyl)-1*H*-phosphirene-*κP*]chromium(0) (12a). Conditions: 100 mg of **1a**, 0.1 mL of toluene, 0.04 mL of ethyl acetylenecarboxylate, 1 h. Crude product **12a**: brown oil; yield over 85%. ^{1}H NMR ($CDCl_3$): *δ* 0.21 (s, 18 H, $SiMe_3$), 0.49 (s br, 1 H, C*H*($SiMe_3$)$_2$), 1.35 (t, ^3J(H,H) = 6.5 Hz, 3 H, CH_2CH_3), 4.36 (q, ^3J(H,H) = 6.5 Hz, 2 H, CH_2CH_3), 9.04 (d, ^2J(P,H) = 21.6 Hz, 1 H, PC*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): *δ* 1.2 (d, ^3J(P,C) = 3.4 Hz, $SiMe_3$), 1.6 (d, ^3J(P,C) = 3.2 Hz, $SiMe_3$), 14.0 (s, OCH_2CH_3), 28.3 (d, ^1J(P,C) = 29.9 Hz, *C*H($SiMe_3$)$_2$), 62.2 (s, OCH_2CH_3), 141.4 (d, $^{(1+2)}J$(P,C) = 20.3 Hz, P*C*), 143.8 (d, $^{(1+2)}J$(P,C) = 14.8 Hz, PCH), 160.9 (d, ^3J(P,C) = 9.0 Hz, *C*O_2Et), 215.6 (d, ^2J(P,C) = 16.0 Hz, *cis*-*C*O), 220.0 (d, ^2J(P,C) = 5.3 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): *δ* −53.8 (s). IR (KBr): *ν̃* 2065 (m), 1943 (vs) cm^{-1} (CO); 1729 (m) cm^{-1} (CO_2).

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-2-(ethoxycarbonyl)-1*H*-phosphirene-*κP*]molybdenum(0)(12b). ^{31}P{^{1}H} NMR (toluene): *δ* −87.1 (s). The product could not be isolated.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-2-(ethoxycarbonyl)-1*H*-phosphirene-*κP*]tungsten(0) (12c). Conditions: 0.3 g of **1c**, 1.5 mL of toluene, 0.1 mL of ethyl acetylenecarboxylate, 1.5 h. **12c**: orange solid; mp 62 °C dec; yield 0.185 g (62%). ^{1}H NMR ($CDCl_3$): *δ* 0.21 (s, 9 H, $SiMe_3$), 0.22 (s, 9 H, $SiMe_3$), 0.63 (d, ^2J(P,H) = 1.4 Hz, 1 H, C*H*($SiMe_3$)$_2$), 1.35 (t, ^3J(H,H) = 7.1 Hz, 3 H, CH_2CH_3), 4.37 (q, ^3J(H,H) = 7.1 Hz, 2 H, CH_2CH_3), 8.95 (d, ^2J(P,H) = 21.7 Hz, 1 H, PC*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): *δ* 1.2 (d, ^3J(P,C) = 3.6 Hz, $SiMe_3$), 1.6 (d, ^3J(P,C) = 3.6 Hz, $SiMe_3$), 14.1 (s, CH_2CH_3), 27.8 (d, ^1J(P,C) = 24.2 Hz, *C*H($SiMe_3$)$_2$), 62.3 (s, CH_2CH_3), 140.5 (d, $^{(1+2)}J$(P,C) = 16.7 Hz, P*C*), 142.7 (d, $^{(1+2)}J$(P,C) = 8.3 Hz, PCH), 160.7 (d, ^3J(P,C) = 9.2 Hz, *C*O_2Et), 196.3 (d, ^2J(P,C) = 8.3 Hz, ^1J(C,W) = 126.4 Hz, *cis*-*C*O), 198.3 (d, ^2J(P,C) = 33.1 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): *δ* −110.8 (s, ^1J(P,W) = 278.4 Hz). MS (70 eV, EI; ^{184}W): *m*/*z* (%) 612 (40) [M$^{\bullet+}$], 528 (60) [(M − 3 CO)$^+$], 472 (90) [(M − 5 CO)$^+$], 444 (80) [(M − 5 CO − C_2H_4)$^+$], 73 (100) [($SiMe_3$)$^+$]. IR (KBr): *ν̃* 2072 (s), 1981 (m), 1943 (vs), 1926 (vs), 1916 cm^{-1} (CO); 1726 (s) cm^{-1} (CO_2). Anal. Calcd for $C_{17}H_{25}NO_7PSi_2W$ (612.4): C, 33.34; H, 4.11. Found: C, 33.65; H, 4.13.

General Procedure for the Synthesis of 2,3-Bis-(methoxycarbonyl)-1*H*-phosphirene Complexes 4a,b. A 1 mmol amount of the 2*H*-azaphosphirene complexes **1a**,**b** was dissolved in 3.0 mL of toluene and 2 mmol (**4a**) or 10 mmol (**4b**) of DMAD. After the solutions were heated at 75 °C for 1.5 h (**4a**) or 3 h (**4b**) with slow stirring, the solutions were evaporated to dryness. Low-temperature chromatography of the residues (SiO_2, 10 × 2 cm, −20 °C, *n*-hexane/diethyl ether 97.5:2.5) afforded the complexes **4a**,**b**, which were crystallized from *n*-pentane at −20 °C.

Pentacarbonyl[1-(bis(trimethylsilyl)methyl)-2,3-bis-(methoxycarbonyl)-1*H*-phosphirene-*κP*)chromium(0) (4a). Conditions: 0.49 g of **1a**, 0.2 mL of DMAD, 75 °C, 1 h. **4a**: yellow solid; mp 87 °C dec; yield 0.30 g (72%). ^{1}H NMR ($CDCl_3$): *δ* 0.16 (s, 18 H, $SiMe_3$), 0.49 (d, ^2J(P,H) = 3.2 Hz, 1 H, C*H*($SiMe_3$)$_2$), 3.86 (s, 6 H, O*C*H_3). ^{13}C{^{1}H} NMR ($CDCl_3$): *δ* 1.1 (d, ^3J(P,C) = 3.3 Hz, $SiMe_3$), 29.6 (d, ^1J(P,C) = 30.5 Hz, *C*H($SiMe_3$)$_2$), 53.1 (s, O*C*H_3), 144.3 (d, $^{(1+2)}J$(P,C) = 19.9 Hz, P*C*), 160.8 (d, ^2J(P,C) = 8.3 Hz, *C*O_2Me), 215.0 (d, ^2J(P,C) =

15.4 Hz, *cis*-*C*O), 219.6 (d, ^2J(P,C) = 4.6 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR (C_6D_6): δ −18.2 (s). MS (70 eV, EI) (^{52}Cr); *m*/*z* (%): 524 (20) [M$^{\bullet+}$], 412 (25) [(M − 4 CO)$^+$], 384 (100) [(M − 5 CO)$^+$], 326 (55) [((OC$_5$)CrPCH(SiMe$_3$)$_2$)$^+$], 73 (30) [(SiMe$_3$)$^+$]. IR (KBr): $\tilde{\nu}$(CO) 2067 (s), 1992 (s), 1962 (vs), 1947 (vs), 1932 (vs), 1921 (vs) cm^{-1}; (CO_2) 1746 (m), 1727 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{25}O_9PSi_2Cr$ (524.5): C, 42.11; H, 4.80. Found: C, 42.21; H, 4.79.

Pentacarbonyl[1-(bis(trimethylsilyl)methyl)-2,3-bis(methoxycarbonyl)-1*H*-phosphirene-κ*P*)molybdenum(0) (4b). Conditions: 0.53 g of **1b**, 1.0 mL of DMAD; 75 °C, 3 h. **4b**: yellow solid; mp 87 °C dec; yield 0.06 g (11%). ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 18 H, SiMe$_3$), 0.60 (d, ^2J(P,H) = 3.8 Hz, 1 H, C*H*(SiMe$_3$)$_2$), 3.91 (s, 6 H, OC*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 1.2 (s, SiMe$_3$), 1.3 (s, SiMe$_3$), 29.3 (d, ^1J(P,C) = 31.4 Hz, *C*H(SiMe$_3$)$_2$), 53.2 (s, O*C*H$_3$), 143.5 (d, $^{(1+2)}J$(P,C) = 20.2 Hz, P*C*), 160.9 (d, ^2J(P,C) = 8.9 Hz, *C*O$_2$Me), 204.3 (d, ^2J(P,C) = 11.0 Hz, *cis*-*C*O), 208.8 (d, ^2J(P,C) = 36.0 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −45.2 (s). MS (70 eV, EI; ^{98}Mo): *m*/*z* (%) 570 (20) [M$^{\bullet+}$], 542 (20) [(M − CO)$^+$], 514 (40) [(M − 2 CO)$^+$], 486 (50) [(M − 3 CO)$^+$], 458 (50) [(M − 4 CO)$^+$], 430 (50) [(M − 5 CO)$^+$], 402 (50) [(M − 6 CO)$^+$], 374 (50) [(M − 7 CO)$^+$], 73 (100) [(SiMe$_3$)$^+$]. IR (KBr): $\tilde{\nu}$(CO) 2076 (s), 1998 (s), 1957 (vs), 1938 (vs), 1923 (vs) cm^{-1}; (CO_2) 1745 (m), 1727 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{25}O_9PSi_2Mo$ (568.5): C, 38.03; H, 4.34. Found: C, 37.22; H, 4.10.

General Procedure for the Synthesis of 5-Alkyl-3,4-bis(methoxycarbonyl)-2*H*-1,2-azaphosphole Complexes 17c,d. A 1.24 g (2 mmol) amount of 2*H*-azaphosphirene tungsten complex **1c** was dissolved either in 6.0 mL of acetonitrile (**17c**) or 4.0 mL of *tert*-butyl cyanide (**17d**), and 0.4 mL (4 mmol) of DMAD was added. After the solutions were heated at 75 °C for 1.5 h with slow stirring, the solutions were evaporated to dryness. Low-temperature chromatography of the residues (SiO_2, 10 × 2 cm, −20 °C, *n*-hexane/diethyl ether 97.5:2.5) afforded the complexes **17c**,**d**, which were crystallized from *n*-pentane at −20 °C.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-3,4-bis(methoxycarbonyl)-5-methyl-2*H*-1,2-azaphosphole-κ*P*]tungsten(0) (17c). 17c: red solid; mp 124 °C dec; yield 0.56 g (41%). ^{1}H NMR ($CDCl_3$): δ 0.13 (s, 9 H, SiMe$_3$), 0.28 (s, 9 H, SiMe$_3$), 1.26 (d, ^2J(P,H) = 9.4 Hz, 1 H, C*H*(SiMe$_3$)$_2$), 2.54 (s, 3 H, C*H*$_3$), 3.86 (s, 3 H, OC*H*$_3$), 3.87 (s, 3 H, OC*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.6 (d, ^3J(P,C) = 2.6 Hz, SiMe$_3$), 3.0 (d, ^3J(P,C) = 2.8 Hz, SiMe$_3$), 19.2 (s, *C*H(SiMe$_3$)$_2$), 21.6 (d, ^3J(P,C) = 16.9 Hz, *C*H$_3$), 52.8 (s, O*C*H$_3$), 53.1 (s, O*C*H$_3$), 139.7 (d, ^1J(P,C) = 27.9 Hz, P*C*C), 163.5 (s, PN*C*), 163.8 (d, $^{(2+3)}J$(P,C) = 2.3 Hz, PC*C*), 164.1 (d, ^3J(P,C) = 1.5 Hz, *C*O$_2$Me), 169.2 (d, ^2J(P,C) = 13.2 Hz, *C*O$_2$Me), 196.6 (d, ^2J(P,C) = 6.5 Hz, ^1J(C,W) = 127.1 Hz, *cis*-*C*O), 198.1 (d, ^2J(P,C) = 23.5 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 104.2 (s, ^1J(P,W) = 238.5 Hz). MS (70 eV, EI; ^{184}W): *m*/*z* (%) 697 (40) [M$^{\bullet+}$], 585 (50) [(M − 4 CO)$^+$], 557 (100) [(M − 5 CO)$^+$], 529 (70) [(M − 6 CO)$^+$], 73 (65) [(SiMe$_3$)$^+$]. IR (KBr): $\tilde{\nu}$ 2072 (s), 1982 (s), 1949 (vs), 1941 (vs), 1923 (vs), 1906 (vs) cm^{-1} (CO); 1734 (s) cm^{-1} (CO_2)**.** Anal. Calcd for $C_{20}H_{28}NO_9PSi_2W$ (697.4): C, 34.43; H, 4.02; N, 2.01. Found: C, 34.37; H, 4.05; N, 1.82.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-3,4-bis(methoxycarbonyl)-5-*tert*-butyl-2*H*-1,2-azaphosphole-κ*P*]tungsten(0) (17d). 17d: red solid; mp 62 °C dec; yield 0.06 g (4%). ^{1}H NMR ($CDCl_3$): δ 0.22 (s, 9 H, SiMe$_3$), 0.23 (s, 9 H, SiMe$_3$), 0.81 (d, ^2J(P,H) = 0.6 Hz, 1 H, C*H*(SiMe$_3$)$_2$), 1.32 (s, 9 H, C(C*H*$_3$)$_3$), 3.86 (s, 3 H, OC*H*$_3$), 3.93(s, 3 H, OC*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.6 (d, ^3J(P,C) = 2.2 Hz, SiMe$_3$), 3.2 (d, ^3J(P,C) = 2.0 Hz, SiMe$_3$), 18.5 (d, ^1J(P,C) = 2.8 Hz, *C*H(SiMe$_3$)$_2$), 28.1 (s, *C*(CH$_3$)$_3$), 40.0 (d, ^3J(P,C) = 13.7 Hz, *C*(CH$_3$)$_3$), 52.7 (s, O*C*H$_3$), 53.1 (s, O*C*H$_3$), 143.2 (d, ^1J(P,C) = 16.0 Hz, P*C*C), 161.7 (s, PN*C*), 162.9 (d, $^{(2+3)}J$(P,C) = 12.6 Hz, PC*C*), 166.2 (d, ^3J(P,C) = 14.8 Hz, *C*O$_2$Me), 178.5 (d, ^2J(P,C) = 15.0 Hz, *C*O$_2$Me), 196.8 (d, ^2J(P,C) = 6.6 Hz, *cis*-*C*O), 198.4 (d, ^2J(P,C) = 23.3 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 97.6 (s, ^1J(P,W) = 238.0 Hz). MS (70 eV, EI), (^{184}W); *m*/*z* (%): 739 (1) [M$^{\bullet+}$], 711 (25) [(M − CO)$^+$], 627 (60) [(M − 4 CO)$^+$], 599 (40) [(M − 5 CO)$^+$], 571 (80) [(M − 6 CO)$^+$], 488 (30) [(M − 6 CO − ^{t}BuCN)$^+$], 460 (35) [(M − 7 CO − ^{t}BuCN)$^+$], 445 (30) [((M − 7 CO − ^{t}BuCN − CH$_3$)$^+$], 73 (100) [(SiMe$_3$)$^+$]. IR (KBr): $\tilde{\nu}$ = 2073 (s), 1989 (s), 1950 (vs), 1923 (vs, sh) 1901 (vs) cm^{-1} (CO); 1745 (s), 1722 (s) cm^{-1} (CO_2); 1583 (m), 1561 (w) cm^{-1} (C═N). Anal. Calcd for $C_{23}H_{34}NO_9PSi_2W$ (739.5): C, 37.36; H, 4.63; N, 1.89. Found: C, 37.27; H, 4.66; N, 1.48.

General Procedure for the Synthesis of 3-(Ethoxycarbonyl)-5-phenyl-2*H*-1,2-azaphosphole Complexes 13a,c. A 1 mmol amount of 2*H*-azaphosphirene complexes **1a**,**c** was dissolved in 3.0 mL of benzonitrile and 0.2 mL (2 mmol) of ethyl acetylenecarboxylate. After the solutions were heated at 75 °C for 1.5 h or at 65 °C for 3.5 h with slow stirring, they were evaporated to dryness. The products **13a**,**c** were separated by low-temperature chromatography of the residues (SiO_2, 12 × 2 cm, −20 °C, *n*-hexane/diethyl ether 97.5:2.5), and the tungsten complex **13c**, additionally, was crystallized from *n*-pentane at −20 °C.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-3-(ethoxycarbonyl)-5-phenyl-2*H*-1,2-azaphosphole-κ*P*]chromium(0) (13a). Conditions: 0.49 g of **1a,** 65 °C, 3.5 h. **13a**: unstable orange oil; yield 0.35 g (62%). ^{1}H NMR ($CDCl_3$): δ 0.13 (s, 9 H, SiMe$_3$), 0.17 (s, 9 H, SiMe$_3$), 1.12 (t, ^3J(H,H) = 7.1 Hz, 3 H, CH$_2$C*H*$_3$), 1.18 (d, ^2J(P,H) = 8.7 Hz, 1 H, C*H*(SiMe$_3$)$_2$), 4.17 (q, ^3J(H,H) = 7.1 Hz, 2 H, C*H*$_2$CH$_3$), 7.36 (m$_c$, 3 H, Ph), 7.59 (m$_c$, 2 H, Ph), 8.38 (d, ^2J(P,H) = 32.4 Hz, 1 H, PCC*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.1 (d, ^3J(P,C) = 2.8 Hz, SiMe$_3$), 2.5 (d, ^3J(P,C) = 1.6 Hz, SiMe$_3$), 13.8 (s, CH$_2$*C*H$_3$), 18.3 (s, *C*H(SiMe$_3$)$_2$), 61.8 (s, *C*H$_2$CH$_3$), 128.1 (s, *m*-Ph), 128.5 (s, *o*-Ph), 130.8 (s, *p*-Ph), 135.3 (d, ^3J(P,C) = 18.4 Hz, *i*-Ph), 138.0 (d, ^1J(P,C) = 22.8 Hz, P*C*CH), 162.1 (d, $^{(2+3)}J$(P,C) = 5.4 Hz, PC*C*H), 164.1 (d, ^3J(P,C) = 17.2 Hz, *C*O$_2$Et), 169.3 (d, $^{(2+3)}J$(P,C) = 10.4 Hz, PN*C*), 215.9 (d, ^2J(P,C) = 12.4 Hz, *cis*-*C*O), 220.7 (d, ^2J(P,C) = 6.6 Hz; *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 138.7 (s). MS (pos.-CI, NH_3; ^{52}Cr): *m*/*z* (%) 584 (100) [(M + H)$^+$], 392 (30) [(M + H − Cr(CO)$_5$)$^+$].

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-3-(ethoxycarbonyl)-5-phenyl-2*H*-1,2-azaphosphole-κ*P*]tungsten(0) (13c). Conditions: 0.62 g of **1c**, 75 °C, 1.5 h. **13c**: orange solid; mp 61 °C dec; yield 0.58 mg (83%). ^{1}H NMR ($CDCl_3$): δ 0.27 (s, 18 H, SiMe$_3$), 1.21 (t, ^3J(H,H) = 7.1 Hz, 3 H, CH$_2$C*H*$_3$), 1.42 (d, ^2J(P,H) = 8.9 Hz, 1 H, C*H*(SiMe$_3$)$_2$), 4.28 (q, ^3J(H,H) = 7.1 Hz, 2 H, C*H*$_2$CH$_3$), 7.47 (m$_c$, 3 H, Ph), 7.67 (m$_c$, 2 H, Ph), 8.41 (d, ^3J(P,H) = 32.7 Hz, 1 H, PCC*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.2 (d, ^3J(P,C) = 2.8 Hz, SiMe$_3$), 2.4 (d, ^3J(P,C) = 1.9 Hz, SiMe$_3$), 13.8 (s, CH$_2$*C*H$_3$), 19.1 (d, ^1J(P,C) = 4.4 Hz, *C*H(SiMe$_3$)$_2$), 61.8 (s, *C*H$_2$CH$_3$), 128.1 (s, *m*-Ph), 128.5 (s, *o*-Ph), 130.8 (s, *p*-Ph), 135.2 (d, ^3J(P,C) = 19.0 Hz, *i*-Ph), 138.0 (d, ^1J(P,C) = 23.5 Hz, P*C*CH), 162.4 (d, $^{(2+3)}J$(P,C) = 9.0 Hz, PC*C*H), 163.8 (d, ^3J(P,C) = 17.2 Hz, *C*O$_2$Et), 170.5 (d, $^{(2+3)}J$(P,C) = 9.6 Hz, PN*C*), 196.3 (d, ^2J(P,C) = 6.4 Hz, ^1J(C,W) = 126.5 Hz, *cis*-*C*O), 198.4 (d, ^2J(P,C) = 21.0 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 94.4 (s, ^1J(P,W) = 227.7 Hz). MS (70 eV, EI; ^{184}W): *m*/*z* (%): 715 (10) [M$^{\bullet+}$], 659 (20) [(M − 2 CO)$^+$], 631 (100) [(M − 3 CO)$^+$], 603 (40) [(M − 4 CO)$^+$], 575 (35) [(M − 5 CO)$^+$], 103 (20) [(C$_7$H$_5$N)$^+$], 73 (70) [(SiMe$_3$)$^+$]. IR (KBr): $\tilde{\nu}$ 2072 (s), 1988 (m), 1927 (vs, sh) cm^{-1} (CO); 1729 (s), 1718 (m) (CO_2) cm^{-1}; 1589 (w, sh), 1561 (w) (C═N) cm^{-1}. HR-EI MS: calcd for $C_{24}H_{30}NO_7PSi_2W$ 715.0807, found 715.0807 ± 2.

Procedure for the Synthesis of Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-3-(ethoxycarbonyl)-5-methyl-2*H*-1,2-azaphosphole-κ*P*]tungsten(0) (13d). A solution of 1.24 g (2 mmol) of 2*H*-azaphosphirene complex **1c** in 6 mL of acetonitrile and 0.4 mL (4 mmol) of ethyl acetylenecarboxylate was heated at 75 °C for 1.5 h with slow stirring. Afterward, the solvent was removed in vacuo and the product was separated by low-temperature chromatography of the residue (SiO_2, 12 × 2 cm, *n*-hexane/diethyl ether 97.5/2.5). The product

could only be obtained as a 1:1 mixture (yellow-brown oil) of the 2*H*-1,2-azaphosphole complex **13d** and 1*H*-phosphirene tungsten complex **12c**.

13d: estimated yield 27% (0.175 g). ^{1}H NMR ($CDCl_3$): δ 0.27 (s, 9 H, $SiMe_3$), 0.31 (s, 9 H, $SiMe_3$), 1.34 (d, ^2J(P,H) = 7.6 Hz, 1 H, C*H*($SiMe_3$)$_2$), 1.46 (t, ^3J(H,H) = 7.1 Hz, 3 H, CH_2CH_3), 2.76 (s, CH_3), 4.43 (q, ^3J(H,H) = 7.1 Hz, 2 H, CH_2CH_3), 8.53 (d, ^3J(P,H) = 32.4 Hz, 1 H, PCC*H*). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 2.2 (d, ^3J(P,C) = 3.0 Hz, $SiMe_3$), 2.6 (d, ^3J(P,C) = 2.3 Hz, $SiMe_3$), 14.2 (s, CH_2CH_3), 18.8 (d, ^1J(P,C) = 4.2 Hz, *C*H($SiMe_3$)$_2$), 23.0 (d, ^3J(P,C) = 19.2 Hz, *C*H_3), 61.7 (s, *C*H_2CH$_3$), 136.8 (d, ^1J(P,C) = 25.8 Hz, P*C*CH), 162.5 (d, ^3J(P,C) = 17.0 Hz, *C*O_2Et), 164.3 (d, $^{(2+3)}J$(P,C) = 9.2 Hz, PC*C*H), 172.8 (d, $^{(2+3)}J$(P,C) = 12.0 Hz, PN*C*), 196.4 (d, ^2J(P,C) = 6.4 Hz, *cis*-*C*O), 198.6 (d, ^2J(P,C) = 20.3 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 90.4 (s, ^1J(P,W) = 227.3 Hz). MS (70 eV, EI; ^{184}W): *m*/*z* (%) 653 (20) [M$^{\bullet+}$], 513 (80) [(M − 5 CO)$^{\bullet+}$], 73 (100) [($SiMe_3$)$^{\bullet+}$].

General Procedure for the Syntheses of 3-(Ethoxycarbonyl)- or/and 4-(Ethoxycarbonyl)-5-(dialkylamino)-2*H*-1,2-azaphosphole Complexes 13e−h and 18b−e, Respectively. Solutions of 1 mmol of 2*H*-azaphosphirene complexes **1a**−**c** (1 mmol of **1c** for **13e** and **18b**) in 3 mL of toluene, 2−5 mmol of ethyl acetylenecarboxylate, and 2 mmol of dialkylamino cyanides were heated at 75 °C for 1.5 (**13e**,**g**,**h** and **18b**,**d**,**e**) or 3 h (**13f** and **18d**) with slow stirring. Afterward, the solvents were removed in vacuo and the products were separated by low-temperature chromatography of the residues (SiO_2, 12 × 2 cm, *n*-hexane/diethyl ether 97.5/2.5) and subsequent crystallization from *n*-pentane at −20 °C.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-3-(ethoxycarbonyl)-5-(dimethylamino)-2*H*-1,2-azaphosphole-κ*P*]tungsten(0) (13e). Conditions: 0.62 g of **1c**, 0.5 mL of ethyl acetylenecarboxylate, 0.2 mL of dimethylamino cyanide, 75 °C, 1.5 h. **13e**: yellow oil; yield 0.48 g (72%). ^{1}H NMR ($CDCl_3$): δ 0.15 (s, 9 H, $SiMe_3$), 0.25 (s, 9 H, $SiMe_3$), 1.18 (d, ^2J(P,H) = 7.5 Hz, 1 H, C*H*($SiMe_3$)$_2$), 1.35 (t, ^3J(H,H) = 7.1 Hz, 3 H, CH_2CH_3), 3.08 (s, 6 H, N(CH_3)$_2$), 4.34 (q, ^3J(H,H) = 7.1 Hz, 2 H, CH_2CH_3), 8.13 (d, ^3J(P,H) = 28.7 Hz, 1 H, PCC*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.3 (d, ^3J(P,C) = 2.4 Hz, $SiMe_3$), 2.6 (d, ^3J(P,C) = 2.2 Hz; $SiMe_3$), 14.1 (s, CH_2CH_3), 22.2 (d, ^1J(P,C) = 4.5 Hz, *C*H($SiMe_3$)$_2$), 39.9 (s, *N*(CH_3)$_2$), 62.1 (s, *C*H_2CH$_3$), 134.6 (d, ^1J(P,C) = 17.7 Hz, P*C*CH), 162.1 (d, $^{(2+3)}J$(P,C) = 5.0 Hz, PN*C*H), 162.3 (d, $^{(2+3)}J$(P,C) = 2,5 Hz, PN*C*), 164.9 (d, ^3J(P,C) = 17.7 Hz, *C*O_2Et), 197.2 (d, ^2J(P,C) = 7.0 Hz, *cis*-*C*O), 200.1 (d, ^2J(P,C) = 20.9 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 78.1 (s, ^1J(P,W) = 239.2 Hz). Anal. Calcd for $C_{20}H_{31}N_2O_7PSi_2Cr$ (696.6): C, 34.49; H, 4.49; N, 2.01. Found: C, 35.02; H, 4.73; N, 1.88.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-4-(ethoxycarbonyl)-5-(dimethylamino)-2*H*-1,2-azaphosphole-κ*P*]tungsten(0) (18b). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 87.6 (s, ^1J(P,W) = 248.9 Hz). The product could not be isolated.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-3-(ethoxycarbonyl)-5-(1-piperidino)-2*H*-1,2-azaphosphole-κ*P*]chromium(0) (13f). Conditions: 0.49 g of **1a**, 0.5 mL of ethyl acetylenecarboxylate, 0.2 mL of 1-piperidinonitrile, 75 °C, 1 h. **13f**: yellow-brown oil; yield 0.11 g (19%). ^{1}H NMR ($CDCl_3$): δ 0.15 (s, 9 H, $SiMe_3$), 0.23 (s, 9 H, $SiMe_3$), 1.07 (d, ^2J(P,H) = 7.4 Hz, 1 H, C*H*($SiMe_3$)$_2$), 1.34 (t, ^3J(H,H) = 7.0 Hz, 3 H, CH_2CH_3), 1,63 (s br, 6 H, $NCH_2CH_2CH_2$), 3.45 (s br, 4 H, $NCH_2CH_2CH_2$), 4.33 (q, ^3J(H,H) = 7.1 Hz, 2 H, CH_2CH_3), 8.25 (d, ^2J(P,H) = 28.6 Hz, 1 H, PCC*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.3 (d, ^3J(P,C) = 2.6 Hz, $SiMe_3$), 2.7 (d, ^3J(P,C) = 2.0 Hz, $SiMe_3$), 14.0 (s, CH_2CH_3), 21.6 (s, *C*H($SiMe_3$)$_2$), 24.4 (s, $NCH_2CH_2CH_2$), 25.7 (s, $NCH_2CH_2CH_2$), 49.0 (s, $NCH_2CH_2CH_2$), 62.0 (s, *C*H_2CH$_3$), 134.9 (d, ^1J(P,C) = 17.4 Hz, P*C*CH), 161.0 (d, $^{(2+3)}J$(P,C) = 3.8 Hz, PN*C*), 162.0 (d, $^{(2+3)}J$(P,C) = 1.6 Hz, PC*C*H), 164.9 (d, ^3J(P,C) = 17.4 Hz, *C*O_2Et), 216.6 (d, ^2J(P,C) = 13.7 Hz, *cis*-*C*O), 221.7 (d, ^2J(P,C) = 7.5 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 121.6 (s). MS (70 eV, EI; ^{52}Cr): *m*/*z* (%) 590 (10) [M$^{\bullet+}$], 478 (60) [(M − 4 CO)$^+$], 450 (100) [(M − 5 CO)$^+$], 73 (20) [($SiMe_3$)$^+$]. Anal. Calcd for $C_{23}H_{35}N_2O_7PSi_2Cr$ (590.7): C, 46.77; H, 5.97; N, 4.74. Found: C, 46.48; H, 5.78; N, 4.61.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-3-(ethoxycarbonyl)-5-(1-piperidino)-2*H*-1,2-azaphosphole-κ*P*]molybdenum(0) (13g). Conditions: 0.53 g of **1b**, 1 mL of ethyl acetylenecarboxylate, 0.2 mL of 1-piperidinonitrile, 75 °C, 3 h. **13g**: yellow-brown solid; mp 66 °C dec; yield 0.145 g (23%). ^{1}H NMR ($CDCl_3$): δ 0.14 (s, 9 H, $SiMe_3$), 0.24 (s, 9 H, $SiMe_3$), 1.02 (d, ^2J(P,H) = 6.1 Hz, 1 H, C*H*($SiMe_3$)$_2$), 1.34 (t, ^3J(H,H) = 7.0 Hz, 3 H, CH_2CH_3), 1,63 (s br, 6 H, $NCH_2CH_2CH_2$), 3.43 (s br, 4 H, $NCH_2CH_2CH_2$), 4.30 (dq, ^3J(H,H) = 7.1 Hz, ^5J(P,H) = 0.3 Hz, 2 H, CH_2CH_3), 8.25 (d, ^3J(P,H) = 29.2 Hz, 1 H, PCC*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.3 (d, ^3J(P,C) = 2.5 Hz, $SiMe_3$), 2.6 (d, ^3J(P,C) = 2.2 Hz; $SiMe_3$), 14.1 (s, CH_2CH_3), 21.7 (s, *C*H($SiMe_3$)$_2$), 24.4 (s, $NCH_2CH_2CH_2$), 25.7 (s, $NCH_2CH_2CH_2$), 49.0 (s, $NCH_2CH_2CH_2$), 61.9 (s, *C*H_2CH$_3$), 134.5 (d, ^1J(P,C) = 18.3 Hz, P*C*CH), 161.7 (d, $^{(2+3)}J$(P,C) = 3.7 Hz, PN*C*), 162.6 (s, PC*C*H), 165.0 (d, ^3J(P,C) = 16.9 Hz, *C*O_2Et), 205.6 (d, ^2J(P,C) = 9.1 Hz, *cis*-*C*O), 210.8 (d, ^2J(P,C) = 22.0 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 99.8 (s). MS (70 eV, EI; ^{96}Mo): *m*/*z* (%) 636 (4) [M$^{\bullet+}$], 608 (20) [(M − CO)$^+$], 580 (70) [(M − 3 CO)$^+$], 496 (70) [(M − 5 CO)$^+$], 494 (100) [(M − C_2H_6 − 4 CO)$^+$], 468 (40) [(M − $C_5H_{10}N$ − 3 CO)$^+$], 73 (100) [($SiMe_3$)$^+$]. IR (KBr): $\tilde{\nu}$ 2070 (s), 1996 (s), 1952 (vs), 1917 (vs, sh) cm^{-1} (CO); 1721 (s) cm^{-1} (CO_2); 1570 (m), 1561 (m) cm^{-1} (C═N). Anal. Calcd for $C_{23}H_{35}N_2O_7PSi_2Mo$ (634.6): C, 43.53; H, 5.56; N, 4.41. Found: C, 43.52; H, 5.62; N, 4.45.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-3-(ethoxycarbonyl)-5-(1-piperidino)-2*H*-1,2-azaphosphole-κ*P*]tungsten(0) (13h). Conditions: 0.62 g of **1c**, 0.5 mL of ethyl acetylenecarboxylate, 0.2 mL of 1-piperidinonitrile, 75 °C, 1.5 h. **13h**: yellow solid; mp 74 °C dec, yield 0.34 g (48%). ^{1}H NMR ($CDCl_3$): δ 0.15 (s, 9 H, $SiMe_3$), 0.25 (s, 9 H, $SiMe_3$), 1.18 (d, ^2J(P,H) = 7.5 Hz, 1 H, C*H*($SiMe_3$)$_2$), 1.34 (t, ^3J(H,H) = 7.1 Hz, 3 H, CH_2CH_3), 1,63 (s br, 6 H, $NCH_2CH_2CH_2$), 3.46 (s br, 4 H, $NCH_2CH_2CH_2$), 4.32 (q, ^3J(H,H) = 7.1 Hz, 2 H, CH_2CH_3), 8.17 (d, ^3J(P,H) = 28.9 Hz, 1 H, PCC*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.3 (d, ^3J(P,C) = 2.5 Hz, $SiMe_3$), 2.6 (d, ^3J(P,C) = 2.2 Hz, $SiMe_3$), 14.1 (s, CH_2CH_3), 22.1 (d, ^1J(P,C) = 4.5 Hz, *C*H($SiMe_3$)$_2$), 24.4 (s, $NCH_2CH_2CH_2$), 25.8 (s, $NCH_2CH_2CH_2$), 49.0 (s, $NCH_2CH_2CH_2$), 62.0 (s, *C*H_2CH$_3$), 134.9 (d, ^1J(P,C) = 18.2 Hz, P*C*CH), 161.9 (d, $^{(2+3)}J$(P,C) = 2.6 Hz, PN*C*), 162.5 (d, $^{(2+3)}J$(P,C) = 5.4 Hz, PC*C*H), 164.8 (d, ^3J(P,C) = 17.8 Hz, *C*O_2Et), 197.2 (d, ^2J(P,C) = 6.9 Hz, ^1J(C,W) = 126.7 Hz, *cis*-*C*O), 200.1 (d, ^2J(P,C) = 20.7 Hz, *trans*-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 77.7 (s, ^1J(P,W) = 239.0 Hz). MS (70 eV, EI; ^{184}W): *m*/*z* (%) 722 (10) [M$^{\bullet+}$], 694 (30) [(M − CO)$^+$], 666 (60) [(M − 2 CO)$^+$], 638 (60) [(M − 3 CO)$^+$], 636 (100) [(M − C_2H_6 − 2 CO)$^+$], 582 (80) [(M − 5 CO)$^+$], 554 (40) [(M − $C_5H_{10}N$ − 3 CO)$^+$], 73 (80) [($SiMe_3$)$^+$]. IR (KBr): $\tilde{\nu}$ 2065 (s), 1972 (m), 1937 (vs, sh), 1925 (vs) 1908 (sh) cm^{-1} (CO); 1720 (s) cm^{-1} (CO_2); 1581 (s), 1561 (m) cm^{-1} (C═N). Anal. Calcd for $C_{23}H_{35}N_2O_7PSi_2W$ (722.5): C, 38.23; H, 4.88; N, 3.87. Found: C, 38.45; H, 4.80; N, 3.70.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-4-(ethoxycarbonyl)-5-(1-piperidino)-2*H*-1,2-azaphosphole-κ*P*]chromium(0) (18c). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 131.7. The product could not be isolated.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-4-(ethoxycarbonyl)-5-(1-piperidino)-2*H*-1,2-azaphosphole-κ*P*]molybdenum(0) (18d). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 108.0. The product could not be isolated.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-4-(ethoxycarbonyl)-5-(1-piperidino)-2*H*-1,2-azaphosphole-κ*P*]tungsten(0) (18e). Conditions: 0.62 g of **1c**, 0.5 mL of ethyl acetylenecarboxylate, 0.2 mL of 1-piperidinonitrile, 75 °C, 1.5 h. **18e**: yellow solid; mp 137 °C dec; yield 0.064 g (9%). ^{1}H NMR ($CDCl_3$): δ 0.04 (s, 9 H, $SiMe_3$), 0.34 (s, 9 H, $SiMe_3$), 1.12 (d, ^2J(P,H) = 5.4 Hz, 1 H, C*H*($SiMe_3$)$_2$), 1.37 (t, ^3J(H,H) =

7.1 Hz, 3 H, CH_2CH_3), 1,66 (s br, 6 H, $NCH_2CH_2CH_2$), 3.65 (s br, 4 H, $NCH_2CH_2CH_2$), 4.36 (m_c, 2 H, CH_2CH_3), 7.53 (d, ^2J(P,H) = 27.1 Hz, 1 H, PC*H*C). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 2.7 (d, ^3J(P,C) = 2.0 Hz, $SiMe_3$), 3.4 (d, ^3J(P,C) = 2.4 Hz, $SiMe_3$), 14.2 (s, CH_2CH_3), 23.0 (d, ^1J(P,C) = 2.0 Hz; *C*H), 24.5 (s, $NCH_2CH_2CH_2$), 25.3−26.9 (m, $NCH_2CH_2CH_2$), 47.6−49.0 (m, $NCH_2CH_2CH_2$), 61.9 (s, CH_2CH_3), 133.8 (d, ^1J(P,C) = 20.1 Hz, P*C*H), 161.0 (d, $^{(2+3)}J$(P,C) = 3.1 Hz, PN*C*), 163.4 (d, $^{(2+3)}J$(P,C) = 3.7 Hz, PCH*C*), 163.8 (d, ^3J(P,C) = 11.3 Hz, CO_2Et), 198.1 (d, ^2J(P,C) = 7.2 Hz, ^1J(C,W) = 127.2 Hz, *cis*-*C*O), 200.3 (d, ^2J(P,C) = 22.5 Hz, *trans*-*C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 86.2 (s, ^1J(P,W) = 248.7 Hz). MS (70 eV, EI; ^{184}W): *m*/*z* (%) 722 (4) [$M^{\bullet+}$], 694 (30) [$(M - CO)^+$], 638 (40) [$(M - 3\ CO)^+$], 582 (100) [$(M - 5\ CO)^+$], 325 (30) [$(M - W(CO)_5 - SiMe_3)^+$], 73 (50) [$(SiMe_3)^+$]. IR (KBr): $\tilde{\nu}$ 2069 (s), 1987 (s), 1938 (vs), 1905 (vs, sh) cm^{-1} (CO); 1712 (m) cm^{-1} (CO_2); 1592 (m), 1529 (m) cm^{-1} (C═N). Anal. Calcd for $C_{23}H_{35}N_2O_7PSi_2W$ (722.5): C, 38.23; H, 4.88; N, 3.87. Found: C, 37.63; H, 4.70; N, 3.83.

Procedure for the Synthesis of (2*H*-1,2-Azaphosphole)-tungsten Complexes 21a,b and Complexes 22a,b and 23a,b. Solutions of 0.62 g of 2*H*-azaphosphirene complex **1c** (1 mmol) in 3 mL of phenylacetylene and 0.2 mL (2 mmol) of dimethyl cyanamide or 1-piperidinonitrile were heated at 75 °C for 1.5 h with slow stirring. Afterward, the solvents were removed in vacuo and the products were separated by low-temperature chromatography of the residues (SiO_2, 12 × 2 cm, *n*-hexane/diethyl ether 97.5/2.5). Evaporation of the second fractions and crystallization from *n*-pentane at −20 °C afforded **21a**,**b**.

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-4-phenyl-5-(dimethylamino)-2*H*-1,2-azaphosphole-κ*P*]tungsten(0) (21a). 21a: pale yellow solid; mp 112 °C dec; yield 70 mg (10%). ^1H NMR ($CDCl_3$): δ 0.21 (s, 9 H, $SiMe_3$), 0.27 (s, 9 H, $SiMe_3$), 1.15 (d, ^2J(P,H) = 8.4 Hz, 1 H, C*H*($SiMe_3$)$_2$), 2.84 (s, 6 H, $N(CH_3)_2$), 7.29−7.47 (m, 5 H, CH_{aromat}), 7.60 (d, ^2J(P,H) = 30.9 Hz, 1 H, PC(*H*)C). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 2.4 (d, ^3J(P,C) = 2.6 Hz, $SiMe_3$), 2.8 (d, ^3J(P,C) = 2.0 Hz, $SiMe_3$), 22.0 (d, ^1J(P,C) = 4.2 Hz, *C*H($SiMe_3$)$_2$), 40.7 (s, $N(CH_3)_2$), 127.6 (s, *m*-Ph), 128.4 (s, *o*-Ph), 128.8 (*p*-Ph), 136.7 (d, ^3J(P,H) = 13.9 Hz, *i*-Ph), 144.7 (d, $^{(2+3)}J$(P,C) = 16.5 Hz, PC(H)*C*), 156.0 (d, ^1J(P,C) = 11.7 Hz, P*C*(H)C), 165.6 (s, PN*C*), 197.8 (d, ^2J(P,C) = 7.2 Hz, *cis*-*C*O), 200.8 (d, ^2J(P,C) = 20.1 Hz, *trans*-*C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 73.1 (s, ^1J(P,W) = 236.8 Hz). IR (KBr): $\tilde{\nu}$ 2066 (s), 1980 (s), 1938 (vs), 1910 (vs) cm^{-1} (CO); 1585 (m), 1571 (s) cm^{-1} (C═N). MS (70 eV, EI; ^{184}W): *m*/*z* (%) 686 (10) [$M^{\bullet+}$], 658 (25) [$(M - CO)^+$], 630 (50) [$(M - 2\ CO)^+$], 602 (25) [$(M - 3\ CO)^+$], 572 (30) [$(M - 4\ CO)^+$], 546 (100) [$(M - 5\ CO)^+$], 73 (20) [$(SiMe_3)^+$]. Anal. Calcd for $C_{23}H_{35}N_2O_7PSi_2W$ (686.5): C, 40.24; H, 4.53; N, 4.08. Found: C, 39.53; H, 4.75; N, 3.78.

Pentacarbonyl[(bis(trimethylsilyl)methyl)(phenylacetylenyl)(*N*-(*C*-(dimethylamino)imino))phosphane]-tungsten(0) (22a). ^{31}P NMR (reaction solution): δ 30.5 (dd, ^2J(P,H) = 29.0, ^2J(P,H) = 5.3, ^1J(P,W) = 259.6 Hz).

Pentacarbonyl[(bis(trimethylsilyl)methyl)(*N*-(*C*-(phenylacetylenyl)-*C*-(dimethylamino)imino))phosphane]tungsten(0) (23a). ^{31}P NMR (reaction solution): δ 17.1 (d, ^1J(P,H) = 311.2, ^1J(P,W) = 249.1 Hz).

Pentacarbonyl[2-(bis(trimethylsilyl)methyl)-4-phenyl-5-(1-piperidino)-2*H*-1,2-azaphosphole-κ*P*]tungsten(0)(21b). 21b: pale yellow solid, mp 119 °C dec; yield 120 mg (17%). ^1H NMR ($CDCl_3$): δ 0.19 (s, 9 H, $SiMe_3$), 0.26 (s, 9 H, $SiMe_3$), 1.24 (d, ^2J(P,H) = 8.4 Hz, 1 H, C*H*($SiMe_3$)$_2$), 1.51 (m_c, 6 H, $NCH_2CH_2CH_2$), 3.20 (m_c, 4 H, $NCH_2CH_2CH_2$), 7.31−743 (m, 5 H, $CH_{aromat.}$), 7.58 (d, ^2J(P,H) = 31.1 Hz, 1 H, PC(*H*)C). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 2.4 (d, ^3J(P,C) = 2.6 Hz, $SiMe_3$), 2.8 (d, ^3J(P,C) = 2.1 Hz, $SiMe_3$), 21.8 (d, ^1J(P,C) = 4.4 Hz, *C*H($SiMe_3$)$_2$), 24.3 (s, $NCH_2CH_2CH_2$), 25.5 (s, $NCH_2CH_2CH_2$), 49.2 (s, $NCH_2CH_2CH_2$), 127.2 (s, *m*-Ph), 128.4 (s, *p*-Ph), 128.8 (*o*-Ph), 136.4 (d, ^3J(P,H) = 13.9 Hz, *i*-Ph), 145.0 (d, $^{(2+3)}J$(P,C) = 16.9 Hz, PC(H)*C*), 155.5 (d, ^1J(P,C) = 12.2 Hz, P*C*(H)C), 165.8 (d, $^{(2+3)}J$(P,C) = 1.3 Hz, PN*C*), 197.7 (d, ^2J(P,C) = 7.2 Hz, *cis*-*C*O), 200.7 (d, ^2J(P,C) = 20.3 Hz, *trans*-*C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 73.4 (s, ^1J(P,W) = 236.4 Hz). IR (KBr): $\tilde{\nu}$ 2065 (s), 1980 (s), 1930 (vs), 1907 (vs) cm^{-1} (CO); 1580 (m), 1565 (s) cm^{-1} (C═N). MS (70 eV, EI; ^{184}W): *m*/*z* (%) 726 (5) [$M^{\bullet+}$], 698 (20) [$(M - CO)^+$], 670 (20) [$(M - 2\ CO)^+$], 640 (30) [$(M - 2\ CO - 2\ Me)^+$], 584 (30) [$(M - 4\ CO - 2\ Me)^+$], 402 (20) [$(M - W(CO)_5)^+$], 73 (100) [$(SiMe_3)^+$]. Anal. Calcd for $C_{26}H_{35}N_2O_5PSi_2W$ (726.2): C, 38.56; H, 4.08; N, 4.91. Found: C, 38.60; H, 4.14; N, 3.81.

Pentacarbonyl[(bis(trimethylsilyl)methyl)(phenylacetylenyl)(*N*-(*C*-(*N*-piperidino)imino))phosphane]tungsten(0) (22b). ^{31}P NMR (reaction solution): δ 30.5 (dd, ^2J(P,H) = 29.0, ^2J(P,H) = 4.2, ^1J(P,W) = 265.4 Hz). IR (1:1 mixture of **21b** and **22b**; toluene): $\tilde{\nu}$ 2163 (w) cm^{-1} (C≡C); 2067 (s), 1973 (s), 1930 (vs) cm^{-1} (CO); 1604 (s) cm^{-1} (C═N).

Pentacarbonyl[(bis(trimethylsilyl)methyl)(*N*-(*C*-(phenylacetylenyl)-*C*-(*N*-piperidino)imino))phosphane]tungsten(0) (23b). 23b: pale yellow solid, mp 158 °C dec; yield 55 mg (8%). ^1H NMR ($CDCl_3$): δ 0.16 (s, 9 H, $SiMe_3$), 0.28 (s, 9 H, $SiMe_3$), 0.73 (dd, ^2J(P,H) = 2.4 Hz, ^3J(H,H) = 1.6 Hz, 1 H, C*H*($SiMe_3$)$_2$), 1.58 (m_c, 6 H, $NCH_2CH_2CH_2$), 3.74 (m_c, 4 H, $NCH_2CH_2CH_2$), 7.36−7.58 (m, 5 H, CH_{aromat}), 7.93 (dd, ^1J(P,H) = 311.4 Hz, ^3J(H,H) = 1.6 Hz, 1 H, P*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.4 (d, ^3J(P,C) = 2.1 Hz, $SiMe_3$), 2.4 (d, ^3J(P,C) = 2.2 Hz, $SiMe_3$), 19.1 (d, ^1J(P,C) = 18.2 Hz, *C*H($SiMe_3$)$_2$), 24.8 (s, $NCH_2CH_2CH_2$), 25.0−27.0 (m, $NCH_2CH_2CH_2$), 43.8 (m_c, $NCH_2CH_2CH_2$), 49.2 (m_c, $NCH_2CH_2CH_2$), 77.4 (d, ^3J(P,C) = 16.6 Hz, N═C*C*≡C), 100.1 (s, N═CC≡*C*), 120.6 (s, *i*-Ph), 128.8 (s, *m*-Ph), 130.2 (s, *p*-Ph), 132.2 (s, *o*-Ph), 143.6 (d, ^2J(P,C) = 8.2 Hz, PN═*C*), 198.1 (d, ^2J(P,C) = 7.5 Hz, *cis*-*C*O), 201.3 (d, ^2J(P,C) = 21.3 Hz, *trans*-*C*O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 16.7 (s, ^1J(P,W) = 249.2 Hz). IR (KBr): $\tilde{\nu}$ 2212 (w) cm^{-1} (C≡C); 2066 (s), 1977 (s), 1936 (vs), 1918 (vs), 1903 (vs) cm^{-1} (CO); 1551 (s) cm^{-1} (C═N). MS (70 eV, EI; ^{184}W): *m*/*z* (%) 726 (5) [$M^{\bullet+}$], 670 (20) [$(M - 2\ CO)^+$], 642 (35) [$(M - 3\ CO)^+$], 614 (40) [$(M - 4\ CO)^+$], 586 (80) [$(M - 5\ CO)^+$], 73 (100) [$(SiMe_3)^+$].

Pentacarbonyl[([bis(trimethylsilyl)methyl)(trimethylsiloxy)phosphane]tungsten(0) (24c). 24c: pale yellow solid; mp 58 °C dec. ^1H NMR ($CDCl_3$): δ 0.13 (s, 9 H, $SiMe_3$), 0.20 (s, 9 H, $SiMe_3$), 0.22 (s, 9 H, $SiMe_3$), 0.79 (dd, ^2J(P,H) = 2.7, ^3J(H,H) = 1.1 Hz, 1 H, PCH), 8.17 (dd, ^1J(P,H) = 325.8, ^{3}J(H,H) = 1.1, ^2J(W,H) = 7.8 Hz, 1 H, PH).). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.35 (d, ^3J(P,C) = 2.5, ^1J(Si,C) = 52.5 Hz, $CSiMe_3$), 0.83 (d, ^3J(P,C) = 1.5, ^1J(Si,C) = 59.8 Hz, $OSiMe_3$), 2.0 (d, ^3J(P,C) = 3.5, ^1J(Si,C) = 52.9 Hz, $CSiMe_3$), 26.6 (d, ^1J(P,C) = 11.3 Hz; *C*H), 197.4 (d, ^2J(P,C) = 7.6 Hz, ^1J(C,W) = 125.9 Hz, *cis*-*C*O), 199.7 (d, ^2J(P,C) = 24.7 Hz, *trans*-*C*O). ^{31}P NMR ($CDCl_3$): δ 76.8 (d, ^1J(P,H) = 326.1, ^1J(P,W) = 275.5 Hz). MS (pos.-CI, isobutane; ^{184}W): *m*/*z* (%) 604 (24) [$M^{\bullet+}$], 576 (2) [$(M - CO)^+$], 281 (100) [$(C_{10}H_{30}OPSi_3)^+$]. IR (KBr): $\tilde{\nu}$ 2071 (s), 1983 (s), 1948 (vs, sh); 1909 (vs) cm^{-1} (CO). Anal. Calcd for $C_{15}H_{29}O_6PSi_3W$ (604.5): C, 29.81; H, 4.84. Found: C, 29.71; H, 4.78.

X-ray Crystallographic Analyses. Structure Determination of 21a. Crystal data: $C_{23}H_{31}N_2O_5PSi_2W$, M_r = 686.50, $P2_1/c$, a = 1011.5(3) pm, b = 1260.8(2) pm, c = 2282.9(3) pm, β = 96.36(2)°, V = 2.8934(10) nm^3, Z = 4, d_{calcd} = 1.576 Mg/m^3, μ = 4.163 mm^{-1}, T = 143 K. A yellow prism (0.70 × 0.35 × 0.20 mm) was mounted in inert oil. A total of 7785 intensities were measured (2θ = 6−50°) using monochromated Mo Kα radiation on a Stoe STADI-4 diffractometer. After absorption correction (ψ-scans) 5098 were unique (R_{int} = 0.0450) and were used for all calculations (program SHELXL-97[39]). Hydrogen atoms were refined as rigid methyl groups with a riding model. The final $R_w(F^2)$ value was 0.0654, with conventional $R(F)$ = 0.0275, for 314 parameters and 51 restraints; the highest peak was 1172 e/nm^3 and deepest hole −880 e/nm^3.

(39) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; Universität Göttingen, Göttingen, Germany, 1997.

Structure Determination of 24c. Crystal data: $C_{15}H_{29}O_6PSi_3W$, $M_r = 604.47$, $P2_1/c$, $a = 937.1(2)$ pm, $b = 1056.8(2)$ pm, $c = 2520.7(5)$ pm, $\beta = 94.65(3)°$, $V = 2.4881(9)$ nm^3, $Z = 4$, $d_{calcd} = 1.614$ Mg/m^3, $\mu = 4.875$ mm^{-1}, $T = 143$ K. A colorless prism (0.50 × 0.40 × 0.40 mm) was mounted in inert oil. A total of 4649 intensities were measured as above. After absorption correction (ψ-scans) 4378 were unique ($R_{int} = 0.0220$) and used for all calculations. The P−H hydrogen was refined with bond length restraints (DFIX), others were treated as detailed above. The final $R_w(F^2)$ value was 0.0749, with conventional $R(F) = 0.0287$, for 248 parameters; the highest peak was 1527 e/nm^3 and deepest hole −842 e/nm^3.

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Supporting Information Available: For **21a** and **24c**, 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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