Table VII. Selected Bond Angles and Torsion Angles (deg) for **5** with Estimated Standard Deviations in Parentheses

S1A-ReA-S2A	89.6 (1)	S1A-ReA-O1A	105.4 (2)
S2A-ReA-O1A	104.3 (2)	S1A-ReA-N11A	87.2 (2)
S2A-ReA-N11A	87.4 (2)	O1A-ReA-N11A	162.7 (3)
S1A-ReA-N21A	162.7 (2)	S2A-ReA-N21A	83.8 (2)
O1A-ReA-N21A	91.7 (3)	N11A-ReA-N21A	76.6 (3)
S1A-ReA-N31A	94.3 (2)	S2A-ReA-N31A	164.7 (2)
O1A-ReA-N31A	89.0 (3)	N11A-ReA-N31A	78.0 (3)
N21A-ReA-N31A	88.2 (3)	ReA-S1A-C41A	112.9 (3)
ReA-S2A-C51A	114.0 (3)	S1B-ReB-S2B	89.9 (1)
S1B-ReB-O1B	105.0 (2)	S2B-ReB-O1B	104.0 (2)
S1B-ReB-N11B	86.3 (2)	S2B-ReB-N11B	86.4 (2)
O1B-ReB-N11B	164.4 (3)	S1B-ReB-N21B	162.7 (2)
S2B-ReB-N21B	83.5 (2)	O1B-ReB-N21B	92.2 (2)
N11B-ReB-N21B	77.3 (3)	S1B-ReB-N31B	94.3 (2)
S2B-ReB-N31B	164.9 (2)	O1B-ReB-N31B	88.9 (3)
N11B-ReB-N31B	79.4 (3)	N21B-ReB-N31B	88.2 (3)
ReB-S1B-C41B	113.4 (3)	ReB-S2B-C51B	116.4 (3)

O1A-ReA-S2A-C51A	-84.84
O1B-ReB-S2B-C51B	-98.87
O1A-ReA-S1A-C41A	-95.14
O1B-ReB-S1B-C41B	-90.52

torsion angles, in Table VII. The compound is monomeric with an approximately octahedral arrangement of the coordination sphere around the rhenium atom. Two distinct molecules of **5** (approximately mirror images of each other) were found in the unit cell as well as 1.5 equiv of CH_2Cl_2. One of the solvent molecules (CH_2Cl_2) was found to be disordered. For complex **5** the average Re=O bond length is 1.668 (5) Å, which is close to the value of 1.689 (5) Å found for complex **4**. The Re-S bonds have a mean length of 2.311 (2) Å, which is also close to the value of 2.301 (2) Å found for **4**. The Re-N bond trans to the oxo ligand has as expected the longest bond length (mean value 2.248 (6) Å), while the other two Re-N bond lengths are shorter, with a mean value of 2.147 (7) Å. All thiolate torsion angles are within 8° of a geometry causing maximal nonbonded repulsions between the filled p_π orbital on sulfur and π-electron density in the Re=O bond. Thus, the large S-Re-O angles (between 104.0 (2) and 105.4 (2)°) can be explained, as was first done for the molybdenum compound $[HB(pz)_3]MoO(SC_6H_5)_2$.[23] The bond lengths and angles found within the $[HB(pz)_3]$ unit show no unusual features and compare well to the values found previously for **1**[2] as well as the values found for **4**.

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Supplementary Material Available: Anisotropic temperature factors and hydrogen atom coordinates for **4** and **5** (Tables SM1, SM2, SM4, and SM5), complete lists of atomic coordinates, bond distances, and bond angles for **5** (Tables SM7-SM9), an ORTEP diagram of the second molecule of **5** (Figure S2), and unit cell diagrams for **4** and **5** (Figures S1 and S3) (18 pages); listings of structure factors for **4** and **5** (Tables SM3 and SM6) (55 pages). Ordering information is given on any current masthead page.

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Primary Alkynylphosphines and Allenylphosphines

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Primary alkynyl- and allenylphosphines are prepared on a gram scale by a chemoselective reduction of the corresponding phosphonates. Their complexation at room temperature leads to the corresponding tungsten pentacarbonyl complexes. Characterization of the phosphines in the free or complexed state was performed by NMR (^1H, ^{31}P, ^{13}C) and infrared spectroscopy and high-resolution mass spectrometry.

Introduction

Compounds containing a divalent or trivalent heteroatom possessing a lone pair of electrons and bonded to one or two hydrogens and to an unsaturated system have been the subject of much interest.[1,2] In condensed phase, they are thermodynamically not stable because of rapid isomerization into the corresponding heteroalkenes or heterocumulenes. However, they are usually kinetically isolable at low temperature by using special techniques or equipment. Simple enols and enamines have been obtained by retro Diels-Alder cleavage under flash thermolytic conditions (FVT).[3,4] Recently, ethynamines were prepared from different precursors by FVT[5] and ethynols were identified by photodecarbonylation of hydroxycyclopropenones in an argon matrix.[6]

The corresponding phosphorus derivatives have been less studied compared to the oxygen or nitrogen analogues. The parent compound ethynylphosphine H-C≡C-PH_2 was analytically prepared for the first time in low yield (9%) by low-pressure electric discharge of an acetylene-phosphine mixture. It was described as a thermally unstable compound, which polymerizes above -20 °C as uncharacterized material.[7] So far only few derivatives stabilized by bulky substituents or complexation have been synthesized.[8] Interestingly, an alkynylphosphine/phospha-allene tautomerism was observed.[9] The potential interest of alkynylphosphines as phosphaallene precursors or ligands in organometallic chemistry prompted us to develop a general approach. As part of our recent interest in the preparation of reactive and unstable molecules containing phosphorus,[10] we recently syn-

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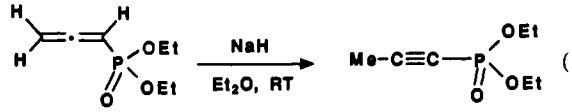
thesized primary vinylphosphines by a chemoselective reduction of the corresponding vinylphosphonates.[11] We show here that the same reduction applied to alkynyl- and allenylphosphonic esters leads to the corresponding primary phosphines. Allenylphosphine derivatives constitute a new class of compounds.

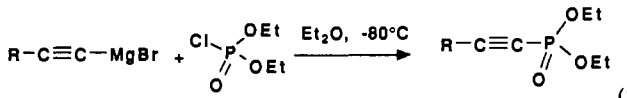
Results and Discussion

Synthesis of Phosphonate Precursors. The alkynylphosphonates **1a–d** were synthesized according to the literature.[12] Compound **1b** was obtained by basic rearrangement of the corresponding allenylphosphonate **2** with NaH[12b] (eq 1). Reaction of an alkynylmagnesium bromide with diethyl phosphorochloridate led to the corresponding alkynylphosphonates **1a**, **c–e**[12a] (eq 2).



(1)

2 **1b**

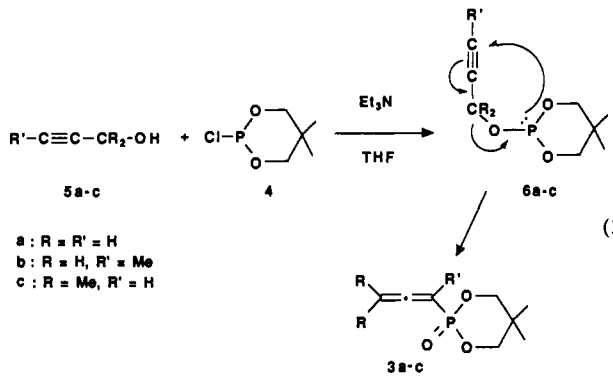


(2)

1a,1c-e

a: R = H, **c**: R = TMS, **d**: R = nBu, **e**: R = Ph

Allenylphosphonates **3a–c** were prepared by condensation of the chlorophosphite **4**[13] on the propargylic alcohol **5a–c** in the presence of Lewis base, followed by a slow rearrangement of the phosphite intermediate **6a–c**[14] (eq 3).



5a-c **4** **6a-c**

(3)

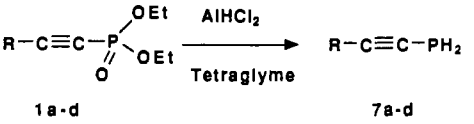
a: R = R' = H
b: R = H, R' = Me
c: R = Me, R' = H

3a-c

Synthesis of Unsaturated Phosphines 7a–e and 8a–c. Unsaturated phosphonates can be reduced in tetraglyme or in diethyl ether and tetrahydrofuran.

Chemoselective reduction of alkynyl- and allenylphosphonates **1a–d** and **3a–c** was performed in tetraglyme at room temperature with an electrophilic reducing agent, the dichloroalane $AlHCl_2$.

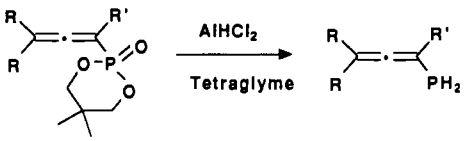
The general procedure already described for the reduction of vinylphosphonates was applied.[11] To limit polymerization, low-boiling unsaturated phosphines were continually evacuated from the reaction mixture and condensed onto a cold trap (77 K) (eqs 4 and 5); yields range from 20 to 48%. The purity of alkynylphosphines **7a–d** was higher than 95%, phosphine PH_3 being the main impurity. Allenylphosphines **8a,c** are contaminated by a small amount of the alkynylphosphine isomers (ca. 10%). When dialkyl allenylphosphonates **9** are used as precursors, the presence of the corresponding alcohol was also observed (ca. 30%).



1a-d **7a-d**

(4)

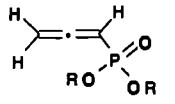
a: R = H, **b**: R = Me, **c**: R = TMS, **d**: R = nBu



3a-c **8a-c**

(5)

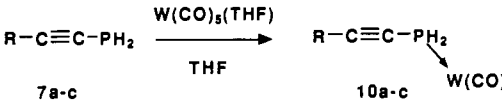
a: R = R' = H
b: R = H, R' = Me
c: R = Me, R' = H



9: R = Me, Et, iPr

The low-temperature reduction (−80 °C) of alkynylphosphonates **1a–e** in ether or THF results in better yield (ca. 80%) with no detectable byproduct. Solvent and phosphines were distilled off in vacuo. Only **7c–e** can be easily separated from the solvent by trap-to-trap distillation. In the case of phosphine **7e**, neutralization of the solution with $NaHCO_3$ before distillation was necessary to minimize polymerization. Reduction of allenylphosphonates **3a–c** under the same conditions leads to a mixture of the corresponding allenyl- and alkynylphosphines.

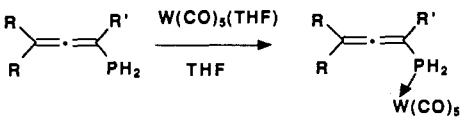
Unsaturated phosphines **7a–e** and **8a–c** can be kept for several weeks in pure form at −20 °C or in diluted solution (ca. 10%) at room temperature in the presence of a small amount of hydroquinone. Complexation of unsaturated phosphines was easily performed with $W(CO)_5THF$ in THF at room temperature. Thus, complexes **10a–c** and **11a–c** were prepared and purified by sublimation (eqs 6 and 7).



7a-c **10a-c**

(6)

a: R = H,
b: R = Me,
c: R = TMS.



8a-c **11a-c**

(7)

a: R = R' = H
b: R = H, R' = Me
c: R = Me, R' = H

The NMR and IR spectra for the free and complexed alkynyl- and allenylphosphines **7**, **8**, **10**, and **11** were recorded at room

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Table I. Selected Spectroscopic Data for Alkynylphosphines **7a–e** and Their Tungsten Pentacarbonyl Complexes **10a–c**[a]

	^{31}P NMR[b]			^{13}C NMR[b]		IR[c]		HRMS ($M^{\bullet+}$)[d]	
compd	δ_P	$^1J_{PH}$	($^1J_{PW}$)	$\delta_{C\equiv CP}$	$\delta_{C\equiv CP}$	$\nu_{C\equiv C}$	ν_{PH}	calcd	found
7a (10a)	−179 (−135)	215 (366)	(233)	91.7 (95.2)	72.4 (71.2)	2205 (2222)	2300 (2338)	57.9972	57.9976
7b (10b)	−176 (−135)	213 (363)	(229)	100.8 (105.9)	64.9 (63.0)	2183 (2205)	2280 (2322)	72.0129	72.0133
7c (10c)	−176 (−139)	215 (364)	(229)	112.7 (118.3)	93.8 (88.8)	2098 (2127)	2288 (2322)	130.0368	130.037
7d	−173	212		105.5	65.4	2185	2283	114.0598	114.060
7e	−176	216		103.1	73.4	2170	2292	134.0285	134.029

[a] Data for complexed phosphines are given in parentheses. [b] $CDCl_3$, TMS, room temperature; J values in Hz. [c] CCl_4, room temperature, ν in cm^{-1}. [d] m/e values.

Table II. Selected Spectroscopic Data for Allenylphosphines **8a–c** and Their Tungsten Pentacarbonyl Complexes **11a–c**[a]

	^{31}P NMR[b]			^{13}C NMR[b]			IR[c]		HRMS ($M^{\bullet+}$)[d]	
compd	δ_P	$^1J_{PH}$	($^1J_{PW}$)	$\delta_{C=C=CP}$	$\delta_{C=C=CP}$	$\delta_{C=C=CP}$	$\nu_{C=C=C}$	ν_{PH}	calcd	found
8a (11a)	−143 (−105)	200 (341)	(230)	71.7 (75.5)	213.2 (215.8)	72.3 (77.9)	1945	2280 (2322)	72.0129	72.0125
8b (11b)	−119 (−83.6)	195 (334)	(229)	70.7 (77.3)	210.3 (212.7)	83.9 (86.3)	1943	2262 (2305)	86.0285	86.0290
8c (11c)	−142 (−103)	197 (334)	(227)	92.9 (99.7)	209.6 (212.8)	77.1 (73.3)	1958	2275 (2320)	100.0446	100.045

[a] Data for complexed phosphines are given in parentheses. [b] $CDCl_3$, TMS, room temperature; J values in Hz. [c] CCl_4, room temperature; ν in cm^{-1}. [d] m/e values.

temperature. They allow an unambiguous structural assignment (Tables I and II). The high value of the coupling constant $^1J_{PH}$ (214 Hz (triplet)) of alkynylphosphines **7** has been already mentioned for the parent compound **7a** and assigned to the strong s character of the phosphorus–hydrogen bond.[7b]

In the infrared spectra, the ν_{P-H} absorption of alkynylphosphines **7** is observed in the narrow-range 2280–2300-cm^{-1} area and $\nu_{C\equiv C}$ is observed between 2170 and 2205 cm^{-1}, except for **7c**, in which the direct attachment of an element with vacant d orbitals leads to a substantial frequency reduction (2098 cm^{-1}).[15] The $\nu_{C=C=C}$ stretching range of 1943–1958 cm^{-1} is typical of allenic derivatives. The influence of complexation on the C≡C and P—H frequencies is weak; the allenic absorption is masked by the intense ν_{CO} stretching.

Experimental Section

Caution! Alkynyl- and allenylphosphines are pyrophoric and nauseative compounds; all preparations and handling must be carried out under a well-ventilated hood.

^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a Brucker AC 300 P spectrometer. Chemical shifts are given in ppm relative to internal $SiMe_4$ for ^{1}H and ^{13}C spectra and external H_3PO_4 for ^{31}P NMR spectra. Chemical shifts upfield of the standard are defined as negative. IR spectra were obtained on a Perkin-Elmer 157G instrument with KBr liquid cells and CCl_4 as solvent (ν in cm^{-1}; s = strong, m = medium, w = weak). High-resolution mass spectra (HRMS) were recorded on a Varian MAT 311 spectrometer. To avoid polymerization, alkynyl- and allenylphosphines are only purified by low-temperature trap-to-trap distillation. They are too reactive to be characterized by combustion analysis.

Alkynylphosphonates were synthesized according to the literature.[12] We have modified the procedure described by Boisselle and Meinhardt[14a] for the preparation of new allenylphosphonates **3a–c**.

Preparation of 5,5-Dimethyl-2-oxo-2-(1,2-dienyl)-1,3,2-dioxaphosphorinanes 3a–c. General Procedure. A 250-mL round-bottomed flask equipped with a magnetical stirring bar is charged under nitrogen with a mixture of 5,5-dimethyl-2-chlorophosphorinane **4** (16.8 g, 0.1 mol), triethylamine (11.1 g, 0.11 mol), and THF (300 mL). Alkynol **5** (0.1 mol) is slowly added at room temperature. The salt (Et_3N·HCl) precipitates. The mixture is then stirred 2 hours. After filtration, the solution is refluxed overnight. The solvents are evacuated in vacuo and the product is purified by crystallization in hexane.

5,5-Dimethyl-2-oxo-2-propa-1,2-dienyl-1,3,2-dioxaphosphorinane (3a). Mp: 132 °C. Yield: 16.5 g (88%). ^{1}H NMR ($CDCl_3$) (δ): 0.98 (s, 3 H), 1.22 (s, 3 H), 4.01 (m, 2 H), 4.03 (m, 2 H), 5.10 (dd, 2 H, $^4J_{HH}$ = 6.5 Hz, $^2J_{PH}$ = 3.5 Hz), 5.40 (td, 1 H, $^4J_{HH}$ = 6.5 Hz, $^4J_{PH}$ = 0.5 Hz). ^{31}P NMR ($CDCl_3$) (δ): 8.8. ^{13}C NMR ($CDCl_3$) (δ): 20.8 ($^1J_{CH}$ = 126 Hz (q)), 21.6 ($^1J_{CH}$ = 125 Hz (q)), 32.5 ($^3J_{CP}$ = 6.5 Hz (d)), 76.5 ($^1J_{CH}$ = 166 Hz (t)), 77.0 ($^2J_{CP}$ = 5.5 Hz (d), $^1J_{CH}$ = 150 Hz (t)), 77.6 ($^1J_{CP}$ = 209 Hz (d), $^1J_{CH}$ = 169 Hz (d)), 214.7. Anal. Calcd for $C_8H_{13}O_3P$: C, 51.06; H, 6.91. Found: C, 51.06; H, 7.05.

5,5-Dimethyl-2-oxo-2-(1-methylpropa-1,2-dienyl)-1,3,2-dioxaphosphorinane (3b). Mp: 102 °C. Yield: 17.6 g (87%). ^{1}H NMR ($CDCl_3$) (δ): 0.97 (s, 3 H), 1.22 (s, 3 H), 1.90 (dt, 3 H, $^3J_{PH}$ = 14.1 Hz, $^5J_{HH}$ = 3.2 Hz), 3.99 (m, 2 H), 4.00 (m, 2 H), 5.00 (dq, 2 H, $^4J_{PH}$ = 13.5 Hz, $^5J_{HH}$ = 3.2 Hz). ^{31}P NMR ($CDCl_3$) (δ): 12.4. ^{13}C NMR ($CDCl_3$) (δ): 20.9 ($^1J_{CH}$ = 127 Hz (q)), 21.7 ($^1J_{CH}$ = 128 Hz (q)), 32.5 ($^3J_{CP}$ = 6.7 Hz (d)), 76.0 ($^3J_{CP}$ = 15.4 Hz (d), $^1J_{CH}$ = 170 Hz (t)), 76.7 ($^2J_{CP}$ = 6.5 Hz (d), $^1J_{CH}$ = 153 Hz (t)), 86.5 ($^1J_{CP}$ = 184 Hz (d)), 211.8 ($^2J_{CP}$ = 6.8 Hz (d)). Anal. Calcd for $C_9H_{15}O_3P$: C, 53.47; H, 7.43. Found: C, 53.57; H, 7.66.

5,5-Dimethyl-2-oxo-2-(3-methylbuta-1,2-dienyl)-1,3,2-dioxaphosphorinane (3c). Mp: 64 °C. Yield: 19.4 g (94%). ^{1}H NMR ($CDCl_3$) (δ): 0.96 (s, 3 H), 1.22 (s, 3 H), 1.80 (dd, 6 H, $^5J_{HH}$ = 3.4 Hz, $^5J_{PH}$ = 7.3 Hz), 3.98 (m, 2 H), 4.02 (m, 2 H), 5.21 (dsext, 1 H, $^2J_{PH}$ = 3.5 Hz, $^5J_{HH}$ = 3.4 Hz). ^{31}P NMR ($CDCl_3$) (δ): 9.9. ^{13}C NMR ($CDCl_3$) (δ): 19.1 ($^4J_{CP}$ = 7.0 Hz (d), $^1J_{CH}$ = 126 Hz (q)), 20.7 ($^1J_{CH}$ = 126 Hz (q)), 21.6 ($^1J_{CH}$ = 127 Hz (q)), 32.3 ($^3J_{CP}$ = 6.6 Hz (d)), 76.3 ($^1J_{CP}$ = 194 Hz (d), $^1J_{CH}$ = 169 Hz (t)), 76.6 ($^2J_{CP}$ = 6.6 Hz, (d), $^1J_{CH}$ = 150 Hz (t)), 97.1 ($^3J_{CP}$ = 16.9 Hz (d)), 210.6. Anal. Calcd for $C_{10}H_{17}O_3P$: C, 55.55; H, 7.87. Found: C, 55.12; H, 8.01.

Preparation of Phosphines 7 and 8. Alkynyl- and allenylphosphines **7** and **8** were obtained by reduction of the corresponding phosphonates. All the reactions were carried out under an inert atmosphere of dry nitrogen by using a two-necked round-bottomed flask equipped with a gas-inlet tube, a rubber septum, and a stirring bar.

Method A: Reduction in Tetraglyme of Alkynylphosphonates 1 and Allenylphosphonates 3. General Procedure (Preparative Scale). The apparatus already described for the reduction of α-chlorophosphonates[11b] was used. Tetraglyme was purified by refluxing over and distilling from sodium/benzophenone under reduced pressure (10^{-2} mbar). The solution of $AlHCl_2$ was prepared according to the procedure recently reported.[11a] The flask containing the reducing mixture (0.5 mol of $AlHCl_2$ in 200 mL of tetraglyme) is fitted to the vacuum line and degassed. Then, the unsaturated phosphonate **1** or **3** (0.1 mol in 50 mL of tetraglyme) is slowly added (30 min) at room temperature with a flexneedle through the septum. During and after the addition, alkynylphosphine or allenylphosphine and the carried away tetraglyme are condensed into a liquid-nitrogen trap. When the reaction is complete (3 h), the cold trap is allowed to warm to room temperature and the volatile species are condensed onto the cold finger (77 K). After disconnection from the vacuum line by stopcocks, the apparatus is filled with gaseous dry nitrogen; liquid nitrogen is subsequently removed. The product is collected in a Schlenk flask and characterized by IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and high-resolution mass spectrometry.

1-Ethynylphosphine (7a). Yield: 40%. ^{1}H NMR ($CDCl_3$) (δ): 2.50 (td, 1 H, $^4J_{HH}$ = 3.2 Hz, $^3J_{PH}$ = 0.8 Hz), 3.65 (dd, 2 H, $^1J_{PH}$ = 215 Hz, $^4J_{HH}$ = 3.2 Hz). ^{31}P NMR ($CDCl_3$) (δ): −179. ^{13}C NMR ($CDCl_3$) (δ): 91.7 ($^1J_{CH}$ = 247 Hz (d), $^3J_{CH}$ = 5.2 Hz (t)), 72.4 ($^1J_{CP}$ = 16 Hz (d)). IR: ν_{CH} 3307 (s), ν_{PH} 2300 (s), $\nu_{C\equiv C}$ 2205 (s). HRMS for $C_2H_3P^{\bullet+}$: calcd, m/e 57.9972; found, m/e 57.9976.

1-Propynylphosphine (7b). Yield: 40%. ^{1}H NMR ($CDCl_3$) (δ): 1.90 (dt, 3 H, $^4J_{PH}$ = 1.3 Hz, $^5J_{HH}$ = 3.1 Hz), 3.63 (dq, 2 H, $^1J_{PH}$ = 213 Hz, $^5J_{HH}$ = 3.1 Hz). ^{31}P NMR ($CDCl_3$) (δ): −176. ^{13}C NMR ($CDCl_3$) (δ): 5.05 ($^1J_{CH}$ = 126 Hz (q)), 64.9 ($^1J_{CP}$ = 7.5 Hz (d)), 100.8 ($^2J_{CP}$ = 2.0 Hz (d)). IR: ν_{PH} 2280 (s), $\nu_{C\equiv C}$ 2183 (s). HRMS for $C_3H_5P^{\bullet+}$: calcd, m/e 72.0129; found: m/e 72.0133.

(15) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1975; p 64.

((Trimethylsilyl)ethynyl)phosphine (7c). Yield: 40%. ^{1}H NMR ($CDCl_3$) (δ): 0.15 (s, 9 H), 3.66 (d, 2 H, $^1J_{PH}$ = 215 Hz). ^{31}P NMR ($CDCl_3$) (δ): −176. ^{13}C NMR ($CDCl_3$) (δ): −0.33 ($^1J_{CH}$ = 120 Hz (q)), 93.8 ($^1J_{CP}$ = 18.9 Hz (d)), 112.7. IR: ν_{PH} 2288 (s), $\nu_{C\equiv C}$ 2098 (s). HRMS for $C_5H_{11}PSi^{\bullet+}$: calcd, *m/e* 130.0368; found, *m/e* 130.037.

1-Hexynylphosphine (7d). Yield: 40%. ^{1}H NMR ($CDCl_3$) (δ): 0.91 (t, 3 H, $^3J_{HH}$ = 7.3 Hz), 1.30–1.60 (m, 4 H), 2.25 (m, 2 H), 3.66 (dt, 2 H, $^1J_{PH}$ = 212 Hz, $^5J_{HH}$ = 3.0 Hz). ^{31}P NMR ($CDCl_3$) (δ): −173. ^{13}C NMR ($CDCl_3$) (δ): 13.5 ($^1J_{CH}$ = 125 Hz (q)), 19.8 ($^1J_{CH}$ = 130 Hz (t)), 21.9 ($^1J_{CH}$ = 117 Hz (t)), 30.4 ($^1J_{CH}$ = 129 Hz (t)), 65.4 ($^1J_{CP}$ = 2.2 Hz (d)), 105.5 ($^2J_{CP}$ = 1.4 Hz (d)). IR: ν_{PH} 2283 (s), $\nu_{C\equiv C}$ 2185 (s). HRMS for $C_6H_{11}P^{\bullet+}$: calcd, *m/e* 114.0598; found, *m/e* 114.060.

Propa-1,2-dienylphosphine (8a). Yield: 30%. ^{1}H NMR ($CDCl_3$) (δ): 3.40 (dm, 2 H, $^1J_{PH}$ = 200 Hz), 4.60 (m, 2 H), 5.28 (m, 1 H, $^2J_{PH}$ = 10.7 Hz). ^{31}P NMR ($CDCl_3$) (δ): −143. ^{13}C NMR ($CDCl_3$) (δ): 71.7 ($^3J_{CP}$ = 6.9 Hz (d), $^1J_{CH}$ = 170 Hz (t)), 72.3 ($^1J_{CH}$ = 168 Hz (d), $^1J_{CP}$ = 11.9 Hz (d)), 213.2 ($^2J_{CP}$ = 14.6 Hz (d)). IR: ν_{PH} 2280 (s), $\nu_{C=C=C}$ 1945 (s). HRMS for $C_3H_5P^{\bullet+}$: calcd, *m/e* 72.0129; found, *m/e* 72.0125.

(1-Methylpropa-1,2-dienyl)phosphine (8b). Yield: 48%. ^{1}H NMR ($CDCl_3$) (δ): 1.90 (dt, 3 H, $^3J_{PH}$ = 4.8 Hz, $^5J_{HH}$ = 3.1 Hz), 3.49 (dt, 2 H, $^1J_{PH}$ = 195 Hz, $^5J_{HH}$ = 3.1 Hz), 4.51 (dtq, 2 H, $^4J_{PH}$ = 4.1 Hz, $^5J_{HH}$ = 3.1 Hz, $^5J_{HH}$ = 3.1 Hz). ^{31}P NMR ($CDCl_3$) (δ): −119. ^{13}C NMR ($CDCl_3$) (δ): 22.8 ($^1J_{CH}$ = 130 Hz (q)), 70.7 ($^1J_{CH}$ = 168 Hz (t), $^3J_{CP}$ = 8.1 Hz (d)), 83.9 ($^1J_{CP}$ = 9.2 Hz (d)), 210.3 ($^2J_{CP}$ = 20.4 Hz (d)). IR: ν_{PH} 2262 (s), $\nu_{C=C=C}$ 1943 (s). HRMS for $C_4H_7P^{\bullet+}$: calcd, *m/e* 86.0285; found, *m/e* 86.0290.

(3-Methylbuta-1,2-dienyl)phosphine (8c). Yield: 20%. ^{1}H NMR ($CDCl_3$) (δ): 1.69 (dd, 6 H, $^5J_{HH}$ = 3.1 Hz, $^5J_{PH}$ = 4.1 Hz), 3.42 (dd, 2 H, $^1J_{PH}$ = 197 Hz, $^3J_{HH}$ = 5.5 Hz), 5.20 (dtsext, 1 H, $^2J_{PH}$ = 12.8 Hz, $^3J_{HH}$ = 5.5 Hz, $^5J_{HH}$ = 3.1 Hz). ^{31}P NMR ($CDCl_3$) (δ): −142. ^{13}C NMR ($CDCl_3$) (δ): 19.7 ($^4J_{CP}$ = 1.9 Hz (d), $^1J_{CH}$ = 128 Hz (q)), 71.1 ($^1J_{CP}$ = 7.7 Hz (d), $^1J_{CH}$ = 170 Hz (t)), 92.9 ($^3J_{CP}$ = 9 Hz (d)), 209.6 ($^2J_{CP}$ = 16 Hz). IR: ν_{PH} 2275 (s), $\nu_{C=C=C}$ 1958 (s). HRMS for $C_5H_9P^{\bullet+}$: calcd, *m/e* 100.0446; found, *m/e* 100.045.

Method B: Reduction of Alkynylphosphonates 1a–c in Diethyl Ether or THF. (a) Procedure Used for Volatile Alkynylphosphines 7a–d. $AlHCl_2$ was prepared by modification of the procedure described by Ashby.[16] Lithium aluminum hydride (4.75 g, 0.125 mol) in dry Et_2O or THF (200 mL) in a 500-mL flask is cooled to −70 °C, and $AlCl_3$ (50 g, 0.375 mol) is quickly added under a nitrogen blanket. The mixture is allowed to warm to 0 °C and immediately used for reduction.[11] Then the flask is cooled to −70 °C and the phosphonate (0.1 mol), diluted in Et_2O or THF (50 mL), is slowly added (20 min). The flask is allowed to warm to 0 °C and fitted to a vacuum line equipped with a cold finger (77 K). The volatile part is condensed onto the cold finger. After disconnection from the vacuum line by stopcocks, the apparatus is filled with gaseous nitrogen, and after the cold finger is heated to room temperature, the solution is collected in a Schlenk flask containing a small amount of hydroquinone (yield 80%). The ether solution of alkynylphosphine **7** can be kept several weeks at 0 °C under neutral atmosphere. Pure phosphines **7c,d** can be obtained by trap-to-trap distillation. For **7a,b** separation from ether being tedious, method A was preferred.

(b) Procedure Used for the Nonvolatile Alkynylphosphine 7e. Nonvolatile alkynylphosphine **7e** cannot be prepared according to method A. Procedure B described above was modified to avoid polymerization during the distillation. After reduction, the solution containing the phosphine is allowed to warm to 0 °C. The decanted solution is then transferred with a flexneedle into a flask containing $NaHCO_3$ (5 g). The mixture is stirred 5 min and transferred into another flask before distillation (pressure 10^{-2} mbar, bath temperature ca. 45 °C). Further purification can be easily performed by trap-to-trap distillation (yield 50%).

(Phenylethynyl)phosphine (7e). Yield: 75%. ^{1}H NMR ($CDCl_3$) (δ): 3.65 (d, 2 H, $^1J_{PH}$ = 216 Hz), 7.24 (m, 3 H), 7.32 (m, 2 H). ^{31}P NMR ($CDCl_3$) (δ): −176. ^{13}C NMR ($CDCl_3$) (δ): 76.4 ($^1J_{CP}$ = 12.3 Hz (d)), 103.1, 122.8, 128.4 ($^1J_{CH}$ = 160 Hz (d)), 128.8 ($^1J_{CH}$ = 162 Hz (d)), 131.7 ($^1J_{CH}$ = 163 Hz (d)). IR: ν_{PH} 2292 (s), ν_{CC} 2170 (s). HRMS for $C_8H_7P^{\bullet+}$: calcd, *m/e* 134.0285; found, *m/e* 134.029.

Preparation of the Complexed Alkynylphosphines 7 and Allenylphosphines 8. A 250-mL Pyrex round-bottomed flask equipped with a magnetic stirring bar is charged with tungsten hexacarbonyl (352 mg, 10^{-3} mol) and THF (70 mL). After 3 h of external irradiation with a medium-pressure mercury lamp, a solution of phosphine **7** or **8** (10^{-3} mol) in 5 mL of THF is added. The mixture is stirred overnight, and then the solvent is removed in vacuo. The complex is purified by sublimation.

(Ethynylphosphine)pentacarbonyltungsten (10a). ^{1}H NMR ($CDCl_3$) (δ): 2.95 (dt, 1 H, $^4J_{HH}$ = 2.5 Hz, $^3J_{PH}$ = 7.9 Hz), 5.51 (dd, 2 H, $^1J_{PH}$ = 366 Hz, $^4J_{HH}$ = 2.5 Hz). ^{31}P NMR ($CDCl_3$) (δ): −135 ($^1J_{PW}$ = 233 Hz, $^1J_{PH}$ = 366 Hz). ^{13}C NMR ($CDCl_3$) (δ): 71.2 ($^1J_{CP}$ = 104 Hz (d)), 95.2 ($^2J_{CP}$ = 13.3 Hz (d), $^1J_{CH}$ = 252 Hz (d)), 194.7 ($^1J_{CW}$ = 134 Hz (d), $^2J_{CP}$ = 7.0 Hz (d), cis CO), 197.3 ($^2J_{CP}$ = 24 Hz (d), trans CO). IR: ν_{CH} 3297 (s), ν_{PH} 2338 (2), $\nu_{C\equiv C}$ 2222 (w), ν_{CO} 2070 (m), 1950 (vs). HRMS for $C_7H_3O_5P^{184}W^{\bullet+}$: calcd, *m/e* 381.9226; found, *m/e* 381.921.

(1-Propynylphosphine)pentacarbonyltungsten (10b). ^{1}H NMR ($CDCl_3$) (δ): 2.06 (dt, 3 H, $^4J_{PH}$ = 3.4 Hz, $^5J_{HH}$ = 2.6 Hz), 5.47 (dq, 2 H, $^1J_{PH}$ = 363 Hz, $^5J_{HH}$ = 2.6 Hz). ^{31}P NMR ($CDCl_3$) (δ): −135 ($^1J_{PW}$ = 229 Hz, $^1J_{PH}$ = 363 Hz). ^{13}C NMR ($CDCl_3$) (δ): 4.95 ($^3J_{CP}$ = 2.3 Hz (d), $^1J_{CH}$ = 132 Hz (q)), 63.0 ($^1J_{CP}$ = 91 Hz (d)), 105.9 ($^2J_{CP}$ = 16.2 Hz (d)), 195.1 ($^2J_{CP}$ = 6.5 Hz (d), $^1J_{CW}$ = 124 Hz (d), cis CO), 198.1 ($^2J_{CP}$ = 23.9 Hz (d), trans CO)). IR: ν_{PH} 2322 (s), $\nu_{C\equiv C}$ 2205 (s), ν_{CO} 2070 (m), 1950 (vs). HRMS for $C_8H_5O_5P^{184}W^{\bullet+}$: calcd, *m/e* 395.938; found, *m/e* 395.938.

(((Trimethylsilyl)ethynyl)phosphine)pentacarbonyltungsten (10c). ^{1}H NMR ($CDCl_3$) (δ): 0.22 (s, 9 H), 5.49 (d, 2 H, $^1J_{PH}$ = 364 Hz). ^{31}P NMR ($CDCl_3$) (δ): −139 ($^1J_{PW}$ = 229 Hz, $^1J_{PH}$ = 364 Hz). ^{13}C NMR ($CDCl_3$) (δ): −0.74 ($^1J_{CH}$ = 118 Hz (q)), 88.8 ($^1J_{CP}$ = 71 Hz (d)), 118.3 ($^2J_{CP}$ = 5.5 Hz (d)), 195.0 ($^1J_{CW}$ = 134 Hz (d), $^2J_{CP}$ = 6.8 Hz (d), cis CO), 197.9 ($^2J_{CP}$ = 24.4 Hz (d), trans CO). IR: ν_{PH} 2322 (s), $\nu_{C\equiv C}$ 2127 (w), ν_{CO} 2070 (m), 1950 (vs). HRMS for $C_{10}H_{11}O_5PSi^{184}W^{\bullet+}$: calcd, *m/e* 453.9621; found, *m/e* 453.965.

(Propa-1,2-dienylphosphine)pentacarbonyltungsten (11a). ^{1}H NMR ($CDCl_3$) (δ): 5.11 (m, 2 H), 5.28 (dtt, 2 H, $^1J_{PH}$ = 341 Hz, $^3J_{HH}$ = 3.8 Hz, $^5J_{HH}$ = 3.3 Hz), 5.63 (m, 1 H). ^{31}P NMR ($CDCl_3$) (δ): −105 ($^1J_{PW}$ = 230 Hz). ^{13}C NMR ($CDCl_3$) (δ): 75.5 ($^1J_{CH}$ = 175 Hz (d), $^1J_{CP}$ = 48 Hz (d)), 77.9 ($^1J_{CH}$ = 170 Hz (t), $^3J_{CP}$ = 14 Hz (d)), 195.3 ($^2J_{CP}$ = 6.9 Hz (d), $^1J_{CW}$ = 125 Hz (d), cis CO), 198.1 ($^2J_{CP}$ = 24 Hz (d), trans CO)), 215.8 ($^2J_{CP}$ = 5.1 Hz (d)). IR: ν_{PH} 2322 (s), ν_{CO} 2070 (m), 1950 (vs). HRMS for $C_8H_5O_5P^{184}W^{\bullet+}$: calcd, *m/e* 395.9382; found, *m/e* 395.939.

((1-Methylpropa-1,2-dienyl)phosphine)pentacarbonyltungsten (11b). ^{1}H NMR ($CDCl_3$) (δ): 2.03 (dt, 3 H, $^3J_{PH}$ = 10.3 Hz, $^5J_{HH}$ = 3.0 Hz), 4.72 (dtq, 2 H, $^4J_{PH}$ = 16.3 Hz, $^5J_{HH}$ = 2.8 Hz, $^5J_{HH}$ = 3.0 Hz), 4.98 (dt, 2 H, $^1J_{PH}$ = 334 Hz, $^5J_{HH}$ = 2.8 Hz). ^{31}P NMR ($CDCl_3$) (δ): −83.6 ($^1J_{PW}$ = 229 Hz). ^{13}C NMR ($CDCl_3$) (δ): 20.7 ($^1J_{CH}$ = 131 Hz (q)), 77.3 ($^1J_{CH}$ = 169 Hz (d)), 86.3 ($^1J_{CP}$ = 45.3 Hz (d)), 195.4 ($^2J_{CP}$ = 7.0 Hz (d), $^1J_{CW}$ = 125 Hz (d), cis CO), 198.3 ($^2J_{CP}$ = 23.8 Hz (d), trans CO)), 212.7 ($^2J_{CP}$ = 14.5 Hz (d)). IR: ν_{PH} 2305 (s), ν_{CO} 2070 (m), 1950 (vs). HRMS for $C_9H_7O_5P^{182}W^{\bullet+}$: calcd, *m/e* 407.9513; found, *m/e* 407.952.

((3-Methylbuta-1,2-dienyl)phosphine)pentacarbonyltungsten (11c). ^{1}H NMR ($CDCl_3$) (δ): 1.74 (dd, 6 H, $^5J_{PH}$ = 7.4 Hz, $^5J_{HH}$ = 3.0 Hz), 5.57 (dtsext, 1 H, $^2J_{PH}$ = 3.2 Hz, $^3J_{HH}$ = 4.2 Hz, $^5J_{HH}$ = 3.0 Hz), 5.19 (dd, 2 H, $^1J_{PH}$ = 334 Hz, $^3J_{HH}$ = 4.2 Hz). ^{31}P NMR ($CDCl_3$) (δ): −103 ($^1J_{PW}$ = 227 Hz). ^{13}C NMR ($CDCl_3$) (δ): 19.6 ($^4J_{CP}$ = 6 Hz (d), $^1J_{CH}$ = 130 Hz (q)), 73.3 ($^1J_{CP}$ = 50 Hz (d), $^1J_{CH}$ = 175 Hz (d)), 99.7 ($^3J_{CP}$ = 15 Hz (d)), 195.4 ($^2J_{CP}$ = 7.1 Hz (d), $^1J_{CW}$ = 125 Hz (d), cis CO), 198.4 ($^2J_{CP}$ = 24 Hz (d), trans CO)), 212.8 ($^2J_{CP}$ = 7 Hz (d)). IR: ν_{PH} 2320 (s), ν_{CO} 2070 (m), 1950 (vs). HRMS for $C_{10}H_9O_5P^{184}W^{\bullet+}$: calcd, *m/e* 423.9695; found, *m/e* 423.970.

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(16) Ashby, E. C.; Hurst, K. M.; Tabaks, J. M. *J. Am. Chem. Soc.* **1966**, *88*, 729.