Reactivity of Organozinc Derivatives of Phosphinines

Herman T. Teunissen and Friedrich Bickelhaupt*

Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

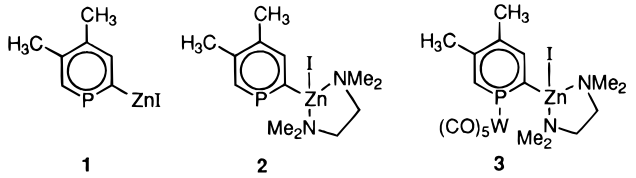
Received September 1, 1995[⊗]

The reactions of the 2-organozinc derivatives **1**, **2**, and **3** of 4,5-dimethylphosphinine with electrophiles of phosphorus, arsenic, tin, copper, silver, and mercury are discussed. The reactions of **2** and **3** with arsenic trichloride furnished the monosubstitution products **4** and **5**, respectively, which were not isolable in pure form. Reactions of **2** and **3** with phosphorus electrophiles were partially successful, but the monosubstitution products **8** and **11**, respectively, were not formed selectively; among the byproducts were **7**, **9**, and **10**. Transmetalation reactions with tin electrophiles gave **13** (37%) and **16** (7%), which were isolated in pure form. Transmetalation of **2** with a copper salt furnished copper derivative **17**, which was trapped below −80 °C with a Michael acceptor and chlorotrimethylsilane to give the 1,4-addition product **19**. This compound was obtained in nearly pure form in a yield of 20% relative to the 2-iodophosphinine **10**. Transmetalation of **3** with a copper salt furnished the copper derivative **20**, which decomposed within 6 h at room temperature. This compound was also prepared via direct insertion of reactive Cu(0) into **12**. Transmetalations with silver salts afforded the organosilver derivatives **21**−**21″**. These silver species turned out to be rather unstable at room temperature. Transmetalation reactions with mercury salts were successful with **1**, **2**, and **3**. The organomercury derivative **22** obtained via **1** and **2**, respectively, decomposed at room temperature, but was characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies. The relatively stable organomercury derivative **23**, obtained from **3**, was isolated in a yield of 50% relative to **10**.

Introduction

The synthesis of phosphinine derivatives, which was first reported by Märkl in 1966,[1] is usually achieved by a multistep procedure in which the phosphinine is prepared from nonphosphaaromatic precursors.[2] During recent years, however, synthetic routes have been developed in which a new phosphinine derivative is prepared by direct functionalization of a halogen-substituted phosphinine. Mathey et al. investigated the synthesis and reactivity of bromo- and chlorophosphinines,[3] whereas our research was focused on the synthesis and reactivity of iodophosphinines.[4] In a previous paper,[4e] we reported the synthesis of 2-iodophosphinines and their pentacarbonyltungsten complexes; furthermore, the synthesis of the organozinc derivatives of phosphinines **1**, **2**, and **3** (Chart 1) was described. These interesting organometallic compounds were prepared

Chart 1



1 **2** **3**

either via insertion of zinc into the carbon−iodine bond of 2-iodo-4,5-dimethylphosphinine in DMF (**1**) or THF/TMEDA (**2**) or, in the case of the pentacarbonyltungsten complex **3**, by reaction of **2** with (acetonitrile)pentacarbonyltungsten (**15**).

In this paper we report the reactions of the organozinc species **1**, **2**, and **3** with PCl_3 and $AsCl_3$ as it is well established that conversion of organozinc derivatives with phosphorus[5] or arsenic[6] electrophiles leads to the corresponding nucleophilic substitution products. In addition, some transmetalations of **1**, **2**, and **3** have been explored; in line with the electronegativity scale of Allred,[7] organometallic derivatives of zinc ($x = 1.6$) can in principle be used for the preparation of organometallic derivatives of tin ($x = 1.96$), mercury ($x = 1.9$), copper ($x = 1.9$), and silver ($x = 1.9$).

Results and Discussion

Reactions with Phosphorus and Arsenic Electrophiles. The reactions of organozinc derivatives of phosphinines with phosphorus and arsenic electrophiles

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

(1) Märkl, G. *Angew. Chem.* **1966**, *78*, 907.

(2) Märkl, G. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme Verlag: Stuttgart, 1990; pp 220−257.

(3) (a) Le Floch, P.; Mathey, F. *Tetrahedron Lett.* **1989**, *30*, 817. (b) Le Floch, P.; Ricard, L.; Mathey, F. *Polyhedron* **1990**, *9*, 991. (c) Le Floch, P.; Carmichael, D.; Mathey, F. *Organometallics* **1991**, *10*, 2432. (d) Le Floch, P.; Carmichael, D.; Mathey, F. *Bull. Soc. Chim. Fr.* **1992**, *129*, 291. (e) Le Floch, P.; Carmichael, D.; Mathey, F. *Phosphorus Sulfur* **1993**, *76*, 33. (f) Le Floch, P.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1993**, 789. (g) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1993**, *115*, 10665. (h) Le Floch, P.; Kolb, A.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 2065. (i) Trauner, H; Le Floch, P.; Lefour, J. M.; Ricard, L.; Mathey, F. *Synthesis* **1995**, 717.

(4) (a) Teunissen, H. T.; Bickelhaupt, F. *Tetrahedron Lett.* **1992**, *33*, 3537. (b) Teunissen, H. T.; Bickelhaupt, F. *Bull. Soc. Chim. Belg.* **1992**, *101*, 609. (c) Bickelhaupt, F. *Pure Appl. Chem.* **1993**, *65*, 621. (d) Teunissen, H. T.; Bickelhaupt, F. *Phosphorus Sulfur* **1993**, *76*, 75. (e) Teunissen, H. T.; Bickelhaupt, F. *Organometallics* **1996**, *15*, 794.

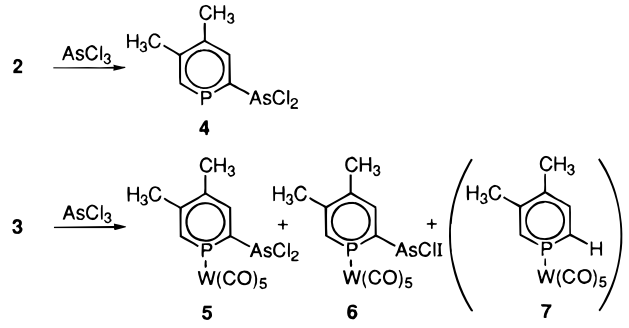
(5) Sasse, K. In *Methoden der Organischen Chemie* (*Houben-Weyl*); Thieme Verlag: Stuttgart, 1963; Vol. 12, No. 1, p 308.

(6) Samaan, S. In *Methoden der Organischen Chemie* (*Houben-Weyl*); Thieme Verlag: Stuttgart, 1978; Vol. 13, No. 8, p 59.

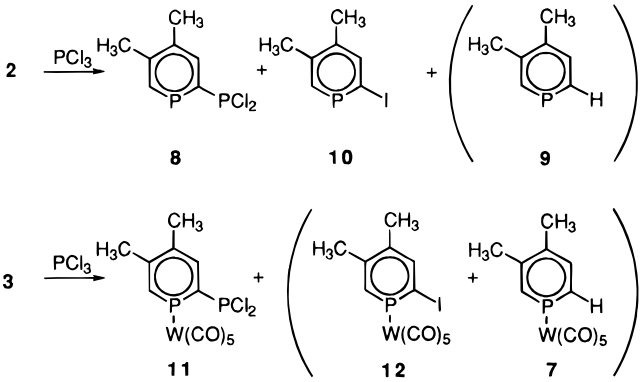
(7) Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.

0276-7333/96/2315-0802$12.00/0

Scheme 1



Scheme 2



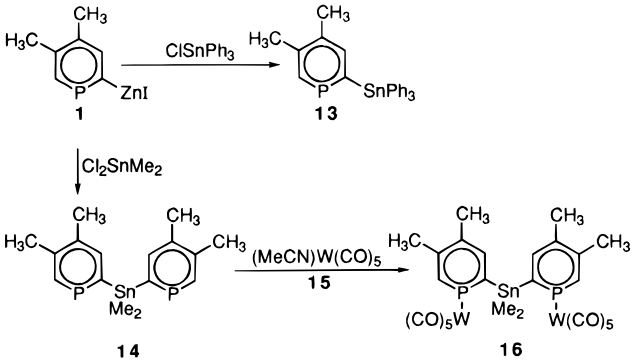
were limited to **2** and **3** and carried out in THF; the inevitable presence of DMF in the reaction mixtures containing **1** makes this organozinc reagent unsuited for reactions with this category of electrophiles as they react with DMF directly. In general, a 6−16-fold excess of freshly distilled ECl_3 (E = P, As) was mixed with THF and cooled to −10 to −60 °C. Then **2** or **3** was added dropwise, after which the reaction mixture was allowed to warm to room temperature.

The reactions of **2** and **3** with $AsCl_3$ are presented in Scheme 1 and showed the expected monosubstitution with the selective formation of **4** ($\delta(^{31}P)$ 198.6 ppm) and **5** ($\delta(^{31}P)$ 165.4 ppm, $^1J(PW)$ = 268.4 Hz), respectively.

The purification of **4** turned out to be difficult as the yellow crystals, initially formed by cooling a pentane extract to −70 °C, slowly decomposed. Therefore, the attention was focused on the purification of **5**. The formation of **5** via **3** was selective and the ratio of **5**:**7** ($\delta(^{31}P)$ 154.8 ppm, $^1J(PW)$ = 268.6 Hz) was 8.6:1, which is satisfactory considering that **7** was already present in the solution of **3** (**3**:**7** = 8.7:1). Crystallization of **5** by cooling a pentane extract to −70 °C did not afford **5** in pure form as **6** ($\delta(^{31}P)$ 159.5 ppm, $^1J(PW)$ = 268.6 Hz) was formed by exchange reactions of **5** with ZnClI. After several unsuccessful purification procedures, the ratio of **5**:**6**:**7** was 188:71:21. Apart from NMR spectra, MS evidence (see Experimental Section) supported the identity of **5** and of the impurities.

The reactions of **2** and **3** with phosphorus electrophiles are presented in Scheme 2. The course of the reaction of **2** with PCl_3 was rather disappointing as formation of **9** and (surprisingly!) **10** accompanied the nucleophilic substitution on phosphorus. Before the reaction with PCl_3, **2** and **9** were present in a ratio of 41:1. After the reaction, **8** ($\delta(^{31}P(Ar))$ 204.8 ppm, $\delta(^{31}P(Cl_2))$ 165.3 ppm, $^2J(PP)$ = 242.4 Hz), **9** ($\delta(^{31}P)$ 192 ppm), and **10** ($\delta(^{31}P)$ 216.4 ppm) were present in a ratio

Scheme 3



of 4:1:1.5, which means that the initial purity of **2** (97.6%) had been reduced to 61.5% in **8**. Mainly because of the presence of **10** (23%), the purification of **8** was rather difficult. Crystallizations from pentane furnished yellow crystals which contained substantial amounts of **10**. The stability of **8** at room temperature was also a problem as an NMR solution of **8** showed slow decomposition.

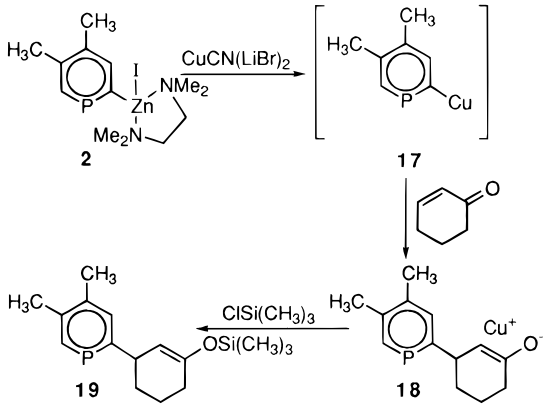
The reaction of **3** with PCl_3 was similarly disappointing as selective formation of a monosubstitution product did not occur. Before the reaction of **3** with PCl_3, **3**, **12** ($\delta(^{31}P)$ 184.6 ppm, $^1J(PW)$ = 280.4 Hz), **9**, and **7** were present in a ratio of 21.8:1.6:1.2:1; afterward, the ratio of **11** ($\delta(^{31}P)$ 174.2 (P(Ar)), 158.4 ($P(Cl_2)$) $^2J(PP)$ = 278.1 Hz, $^1J(PW)$ = 273.8 Hz):**12**:**9**:**7**, was 1.3:0.2:0.2:1. This implies 85% relative abundance of **3** before the reaction and 48% of **11** after the reaction. As **12** was already present in the metallation mixture of **3**, it is difficult to ascertain whether it was also formed during the reaction with PCl_3. Nevertheless, the low relative abundance of **11** (48%) made the reaction unattractive for preparative purposes. Altogether, it is difficult to mechanistically explain the rather disappointing behavior of **2** and **3** in reactions with PCl_3.

Transmetalations with Tin Derivatives. These reactions have been carried out predominantly with **1** and only incidentally with **2** and **3**. The transmetalations with **1** were focused on reactions with $ClSnPh_3$ and $Cl_2Sn(CH_3)_2$ (Scheme 3).

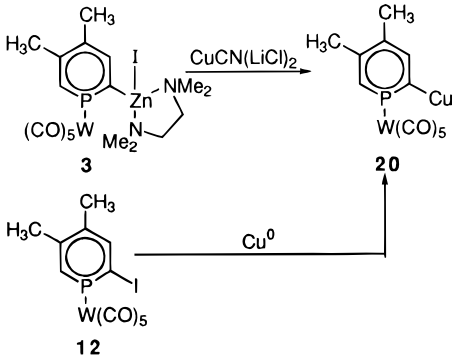
The reaction of **1** with $ClSnPh_3$ at room temperature afforded **13** ($\delta(^{31}P)$ 222.0 ppm, $^2J(P^{119}Sn)$ = 317.3 Hz); it was the only detectable phosphorus containing product, but it was isolated in 37% yield only. In solution, **13** decomposes slowly with concomitant formation of a yellow precipitate. This slow decomposition explains the moderate yield and the slight deviations in the elemental analysis (see Experimental Section). Mathey et al. reported similar problems with functionalized phosphinines.[3c]

The reaction of **1** with $Cl_2Sn(CH_3)_2$ was performed to obtain **14**, which was expected to possess bidentate coordinating properties. The isolation of **14** ($\delta(^{31}P)$ 218.5 ppm, $^2J(P^{119}Sn)$ = 330.8 Hz) in pure form was difficult as decomposition with concomitant formation of a yellow precipitate was substantially faster than in the case of **13**. Therefore, **14** was transformed into its $W(CO)_5$ complex by reaction with (acetonitrile)pentacarbonyltungsten (**15**). In this way, **16** ($\delta(^{31}P)$ 176.8 ppm, $^1J(PW)$ = 262.8 Hz, $^2J(P^{119}Sn)$ = 213.5 Hz) was isolated in pure form. It was obtained in a yield of 7% relative to $Cl_2Sn(CH_3)_2$ and fully characterized. The low yield of **16** does

Scheme 4



Scheme 5

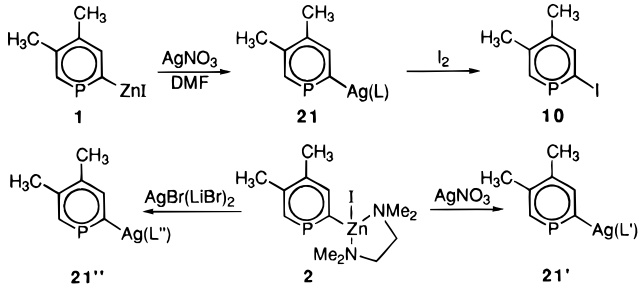


not reflect the real yield of **14** in view of the numerous manipulations.

Transmetalations with Copper Salts. Transmetalations of **2** and **3** with copper salts showed that the organocopper derivatives were rather unstable. As shown in Scheme 4, the organocopper phosphinine **17** was formed in situ at −80 °C. A solution of **2** was reacted with a THF solution of CuCN·2LiBr, which also contained 2-cyclohexen-1-one and $ClSi(CH_3)_3$. By Michael addition of **17**, which in a separate experiment was shown not to occur in reaction with **2** alone, the enolate **18** was formed and converted directly to the silyl ether **19** ($\delta(^{31}P)$ 190.2 ppm) by $ClSi(CH_3)_3$. Together with **19**, an appreciable amount of **9** (Scheme 2) was formed. The purification of **19** was difficult, not only because of the presence of **9**, but mainly due to the presence of zinc and copper salts and their TMEDA complexes (see Experimental Section). After purification, nearly pure **19** was obtained as a brown oil in a yield of 20% relative to **10**, the precursor of **2**. The purity of **19** was not 100%; the ^1H NMR spectrum showed the presence of traces of **9** and several signals between 0 and 2 ppm not belonging to **19**. Therefore, the $\delta(^1H)$ of the aliphatic protons of **19** was determined from its CH COSY spectrum. The lack of purity was also evident from the elemental analysis, in which the experimental value for carbon was 2.08% higher than the calculated one.

The reaction of **3** with a THF soluble copper salt at −60 °C furnished **20** ($\delta(^{31}P)$ 171.2 ($^1J(PW) = 249.9$ Hz)) which, together with **7**, was present in a ratio of 13.3:1 (Scheme 5). Before the reaction, the ratio of **3** to **7** was 18.8:1. Compound **20** decomposed completely at room temperature within 6 h; in the ^{31}P NMR spectrum, two new signals appeared around 55 ppm and one at 37 ppm. In an alternative approach, **20** was obtained by

Scheme 6[a]



[a] In structures **21**, L, L′, or L″ indicates coordination of solvent or Lewis base, which in an unidentified fashion depends on the system used.

reaction of **12** with in situ prepared, highly reactive metallic copper, in analogy with a procedure developed by Rieke.[8] A ^{31}P NMR spectrum of the crude reaction mixture showed the presence of **20** ($\delta(^{31}P)$ 171 ppm, $^1J(PW) = 244$ Hz), **7**, and a component with $\delta(^{31}P)$ 227 ppm, in a ratio of 10.6:1:2.6. The decomposition of **20**, obtained from **3** or **12**, proceeded in a similar fashion.

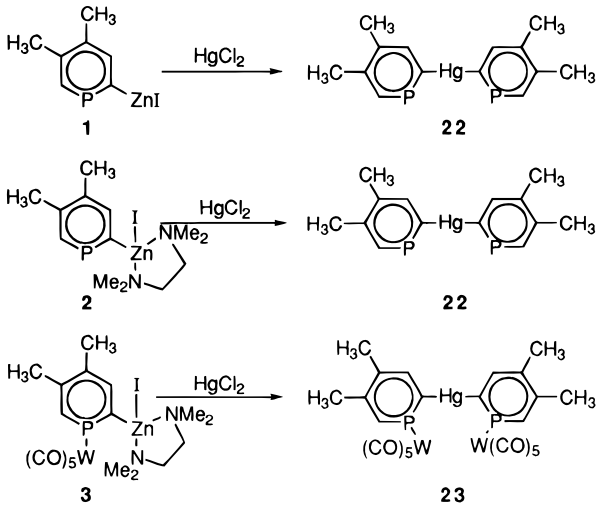
Transmetalations with Silver Salts. Transmetalations of **1**, **2**, and **3** with silver salts were carried out with limited success, as the organosilver derivatives were unstable at room temperature. Whereas the transmetalation of **3** with the THF-soluble salt AgBr·2LiBr resulted in decomposition of **3**, the transmetalations involving **1** and **2** were more successful (Scheme 6).

The transmetalation of **1** was achieved with $AgNO_3$ at room temperature. The solution became black, and a grey precipitate was formed. The ^{31}P NMR spectrum showed, apart from small amounts of **9** and **10** in a ratio of 1:0.29, two large, broad signals at 208 ppm (line width 100 Hz) and 194 ppm (line width 120 Hz) in a ratio of 3.4:1.0, which are assigned to two forms of **21**. The organosilver derivatives were thermally stable at −20 °C, whereas at room temperature, decomposition occurred rather quickly with concomitant formation of a grey precipitate. The formation of **21** was supported by a quench reaction with iodine, which furnished **10**; after this quench reaction, the ratio **9**:**10** was 1:15.2. This does not unambiguously prove that Ag is bonded to the 2-position of the phosphinine ring, as **1** would show the same reaction with iodine while the new ^{31}P NMR signals could be due to the formation of η^1-P−Ag complexes. The arguments in favor of the formation of **21** are that silver nitrate is frequently used in transmetalation reactions of organozinc compounds to give the corresponding organosilver species.[9] Furthermore, the low thermal stability of **21** suggests the presence of an organosilver species, as **1** is thermally very stable. A conceivable alternative for the transmetalation is the formation of an η^1-Ag complex of **1**. However, η^1-coordination of a phosphinine to Ag has been reported to give stable complexes.[10]

The transmetalation of **2** was carried out with $AgNO_3$ and with the THF-soluble salt AgBr·2LiBr; it showed remarkable differences from that of **1** (Scheme 6). Only

(8) Stack, D. E.; Dawson, B. T.; Rieke, R. D. *J. Am. Chem. Soc.* **1991**, *113*, 4672.
(9) van Koten, G.; Noltes, J. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 2, p 709 vv.
(10) Kanter, H.; Dimroth, K. *Tetrahedron Lett.* **1975**, 541.

Scheme 7



one broad signal (line width 50−70 Hz) of the organosilver derivatives **21′** (δ(^{31}P) 199 ppm) and **21″** (δ(^{31}P) 200 ppm), respectively, was observed. Westmijze et al. reported that the use of AgBr·2LiBr suppresses the decomposition of organosilver compounds.[11] They suggested that LiBr is built into the alkylsilver clusters by analogy of the stabilizing influence of CuBr on some arylcopper cluster compounds. In our case, a stabilizing influence of LiBr on **21″** relative to **21′** was not observed. The ratio **21′**:**9** decreased within 50 min at room temperature from 2.8:1 to 1.7:1. The analogous ratio of **21″**:**9** decreased from 3:1 to 1.9:1 under the same conditions. The decomposition of **21″** was followed at 4 °C by ^{31}P NMR spectroscopy, which indicated that the decomposition with concomitant formation of **9** was complete within 5 days. Organosilver derivative **21″** was also characterized by ^{13}C NMR spectroscopy at −25 °C. The signals originating from **21″** were distinguished from those of **9** as the signals of **21″** disappeared upon standing.

Transmetalations with Mercury Salts. The transmetalations reactions of **1**, **2**, and **3** with mercury salts were the only category of transmetalations for which all organozinc derivatives provided unambiguous positive results (Scheme 7).

In the reaction of **1** with $HgCl_2$ at room temperature, a colorless precipitate was formed quickly and the ^{31}P NMR spectrum showed the presence of **22** (δ(^{31}P) 213.1 ppm, ^2J(PHg) = 797 Hz), **1**, and small amounts of **9** and **10** in the dark red solution. The ratio of **22**:**9** was 11.7:1. After evaporation of DMF under vacuum, the residue was extracted with toluene. After removal of toluene under vacuum, the residue was extracted with C_6D_6 after which **22** was characterized by ^{1}H and ^{31}P NMR spectroscopy. It turned out to be unstable at room temperature; decomposition was complete within several hours. This decomposition is possibly catalyzed by zinc salts such as ZnICl·$(DMF)_2$. Their presence was indicated by ^{1}H NMR signals of DMF which were shifted relative to those of free DMF (see Experimental Section); note that zinc,[12,13] contrary to mercury,[14] is known to coordinate to DMF.

The stability of **22**, prepared from **2**, was completely different from that of **22**, prepared from **1**. A solution of **2** was cooled to −60 °C; then TMEDA and finally solid $HgCl_2$ (0.5 equiv) were added. Next, the reaction mixture was warmed slowly to room temperature, during which a brown precipitate was formed. Subsequent ^{31}P NMR analysis showed the presence of **22** (δ(^{31}P) 212.8 ppm, ^2J(PHg) = 786.1 Hz) and **9** in a ratio of 10:1. After 2 h at room temperature, this ratio had decreased to 5:1. After the addition of pentane (THF:pentane = 1:1), more precipitate was formed. The supernatant was separated and cooled to −70 °C. After cooling, the extract showed the formation of light brown crystals, contaminated with some grey material. The crystals of **22** were analyzed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies. Compound **22** decomposed slowly in the $CDCl_3$ solution: approximately 15% in 4 days. The ^{13}C NMR spectrum of **22** strongly supported its structural composition. The signal of C2 (194.7 ppm) was a double doublet with ^1J(PC) = 79.4 Hz and ^3J(PC) = 7.2 Hz. This indicates the connection of two phosphinine moieties via C2 and is only compatible with the structure assignment of **22**; the conceivable alternative, i.e., the formation of a monoarylated mercury chloride (RHgCl), is excluded. The proton spectra of **22** showed the presence of TMEDA signals which were deshielded relative to a reference sample of TMEDA in $CDCl_3$: 0.40 ppm for the methyl groups and 0.36 ppm for the methylene groups. In view of the known differences between zinc[15] and mercury[16] in their complexing ability toward TMEDA, these signals may confidently be assigned to zinc salt complexes. The molar ratio of TMEDA:**22** was 1.5:1, thus indicating the presence of an appreciable amount of zinc salts, which were also observed in the mass spectra. Presumably these salts play a role in the thermal decomposition of **22**.

As the goal of an isolable organomercury derivative of a phosphinine derivative was not yet achieved, the attention was focused on the synthesis of **23**, the pentacarbonyltungsten complex of **22**. As shown in Scheme 7, **23** was prepared by the reaction of $HgCl_2$ with **3** at 0 °C. Compound **23** (δ(^{31}P) 175.1 ppm, ^1J(PW) = 261.6 Hz, ^2J(PHg) = 627.7 Hz) was isolated in pure form. The purification was simple as **23** precipitated from the reaction mixture and washing with THF removed all zinc salts. This compound was also characterized with (HR)MS spectroscopy; it showed a molecular ion with the appropriate isotope pattern. In the mass spectrum, zinc salts were absent, indicating that the removal of zinc salts in the purification of **23** is no problem. The stability of **23** is higher than that of **22**, probably due to the absence of zinc salts. Nevertheless, the light yellow green powder became inhomogeneous after a few weeks storage at 4 °C as some grey material was formed. In spite of the slow decomposition, the results of the elemental analysis of **23** were very good and in agreement with the proposed composition.

Conclusions

The reactions of organozinc derivatives **2** and **3** with PCl_3 or $AsCl_3$ furnished the expected monosubstitution

(11) Westmijze, H.; Kleijn, H.; Vermeer, P. *J. Organomet. Chem.* **1979**, *172*, 377.
(12) Ishiguro, S.; Ozutsumi, K.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 531.
(13) Goggin, P. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1987; Vol. 2, p 491.
(14) Dean, P. A. W. *Prog. Inorg. Chem.* **1978**, *24*, 109.
(15) Armstrong, R. S.; Aroney, M. J.; Duffin, R. K.; Stootman, H. J.; Le Fèvre, R. J. W. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1272.
(16) Bell, N. A.; Nowell, I. W.; Reynolds, P. A.; Lynch, R. J. *J. Organomet. Chem.* **1980**, *193*, 147.

Table 1. ^{1}H NMR Data of 2-R-4,5-Dimethylphosphinines[a]

		4-CH_3			H3		H6	
no.	R	δ (ppm)	^5J(PH) (Hz)	5-CH_3 δ (ppm)	δ (ppm)	^3J(PH) Hz)	δ (ppm)	^2J(PH) (Hz)
19	R_1[b]	2.03	3.1	2.04	7.55	6.2	8.34	38.3
8	PCl_2	1.72	3.5	1.77	8.12	5.7	8.01	40.4
4	$AsCl_2$	1.74	3.5	1.81	8.11	6.0	7.99	40.8
5	$AsCl_2$[c]	1.64	5.9	1.53	8.31	19.9	7.54	27.7
13	$SnPh_3$	1.86	3.4	2.00	8.13	12.3	8.48	36.0
14	$SnMe_2$	1.95	3.3	1.99	8.10	12.8	8.45	35.7
16	$SnMe_2$[c]	1.82	6.2	1.74	7.75	29.8	8.23	24.0
22	Hg[d]	2.04	3.5	2.09	7.50	15.3	8.62	34.4
22	Hg[e]	2.35	3.5	2.43	7.89	14.8	8.67	34.5
23	Hg[c,f]	2.36	6.2	2.46	7.95	32.5	8.52	22.8

[a] C_6D_6 was used as solvent unless otherwise stated. [b] R_1 refers to the 3-(trimethylsiloxy)-2-cyclohexen-1-yl substituent. The numbering of the phosphinine ring is adapted to that of other phosphinines and differs from the numbering in the experimental part. [c] P-$W(CO)_5$ complex. [d] Prepared from **1**. [e] Prepared from **2**, NMR in $CDCl_3$. [f] NMR in THF-d_8.

Table 2. ^{13}C NMR Data of 2-R-4,5-dimethylphosphinines[a]

		C2		C6		C3		C5		C4		4-CH_3		5-CH_3	
no.	R	δ (ppm)	^1J(PC) (Hz)	δ (ppm)	^1J(PC) (Hz)	δ (ppm)	^2J(PC) (Hz)	δ (ppm)	^2J(PC) (Hz)	δ (ppm)	^3J(PC) (Hz)	δ (ppm)	^4J(PC) (Hz)	δ (ppm)	^3J(PC) (Hz)
19	R_1[b]	177.7	47.9	154.8	49.9	136.3	12.8	141.2	15.8	138.7	17.2	22.4	2.2	22.9	3.4
8	PCl_2	167.0	63.0	154.3	57.2	139.3	12.6	147.5	13.4	140.1	17.2	21.7	1.9	23.1	3.6
4	$AsCl_2$	*c*	*c*	154.1	58.9	140.1	18.7	*c*	*c*	*c*	*c*	21.7	1.9	23.0	3.4
5	$AsCl_2$[d]	151.7	15.5	149.0	18.1	142.2	15.7	145.0	15.4	138.7	28.9	21.4	3.7	22.9	9.8
13	$SnPh_3$	163.9	79.2	156.7	61.0	144.9	15.0	144.1	14.5	138.6	24.8	22.0	1.7	23.3	2.7
14	$SnMe_2$	167.7	80.1	156.5	61.3	143.8	14.2[e]	143.5	14.5[f]	138.0	25.6	22.1	*g*	23.4	*g*
16	$SnMe_2$[d]	161.3	24.5	154.0	11.0	147.5	21.0	148.5	15.8	136.6	35.8	21.7	4.2	22.9	8.4
21″	Ag[h]	177.7	74.5	152.4	30.6	149.3	22.0	142.8	16.6	136.1	36.8	23.8	*g*	22.5	12.8
22	Hg[i]	194.7	79.4	155.4	60.7	144.3	15.2	143.7	14.8	138.7	26.4	22.5	2.0	23.4	2.7
23	Hg[d,j]	*c*	*c*	151.0	8.2	148.1	20.8	147.8	15.9	136.9	37.4	22.0	*g*	22.2	8.2

[a] NMR in C_6D_6 unless otherwise mentioned. [b] R_1 refers to the 3-(trimethylsiloxy)-2-cyclohexen-1-yl substituent. The numbering of the phosphinine ring is adapted to that of the other phosphinines and differs from the numbering in the experimental part. [c] Quaternary aromatic carbon atom(s) not detectable. [d] P−$W(CO)_5$ complex. [e] AXX′ system: $^2J(PC) + {}^4J(PC) = 14.2$ Hz. [f] AXX′ system: $^2J(PC) + {}^6J(PC) = 14.5$ Hz. [g] Too small to be detected. [h] NMR in THF. [i] Prepared via **2**, NMR in $CDCl_3$. [j] NMR in THF-d_8.

products. Due to limited stability of the products and/or the formation of byproducts none of the functionalized phosphinines could be isolated in pure form. The transmetalations of **1**, **2**, and **3** with tin, copper, silver, and mercury derivatives were successful, although the thermal lability of the products in several cases hampered their isolation and characterization. The organocopper and organosilver derivatives were less well characterized; the organotin and organomercury derivatives were isolable as their pentacarbonyltungsten complexes and showed sufficient, but not absolute, thermal stability under ordinary conditions.

A general conclusion from both our results and those of Mathey et al.[3c] may be that functionalized phosphinines appear to be less stable than initially expected. The reasons for this are not clear at the moment.

Experimental Section

General Procedures. All oxygen- and/or water-sensitive reactions were carried out under dry nitrogen with oven-dried glassware and oxygen-free, dry solvents. THF was distilled first from NaH and finally from Na/benzophenone. Pentane was distilled from $LiAlH_4$. PCl_3, chlorotrimethylsilane, and $AsCl_3$ were distilled before use. LiCl and LiBr were dried by heating under vacuum. The starting compound (acetonitrile)-pentacarbonyltungsten[17] was prepared according to a reported procedure.

NMR spectra were recorded at a Bruker AC 200 spectrometer at 200 MHz (^{1}H) or 50.32 MHz (^{13}C). For ^{31}P NMR spectroscopy, a Bruker WM 250 was used operating at 100.26 MHz. ^{1}H, ^{13}C, or ^{31}P NMR experiments were carried out with a Bruker MSL 400, operating at 400 (^{1}H), 100.64 (^{13}C), or 161.9 MHz (^{31}P). The coupling constants (J) are given in hertz. The diagnostic data are collected in Table 1 (^{1}H) and Table 2 (^{13}C). The assignments are based on routine 2D NMR techniques.

Ratios of different phosphinines present in reaction mixtures were determined from the relative intensities of their ^{31}P NMR signals. This is justified as these phosphinine derivatives are structurally so closely related that they may be expected to have a similar relaxation behavior.

The direct inlet mass spectra were measured with a Finnigan MAT 90 (Bremen, FRG), Source temperature 150 °C (70 eV IP). The GC/MS spectra were measured with a Hewlett-Packard 5970 MSD equipped with a 5890 GC with 50 m CP Sil 5CB column. In the mass spectra, the appropriate isotope pattern was observed unless otherwise stated.

Elemental analyses were carried out by Micro Analytisches Labor Pascher (Remagen, Germany). Melting points (uncorrected) were determined with melting point equipment of Pleuger after Dr. Tottoli.

2-(Dichloroarsino)-4,5-dimethylphosphinine (4). A solution of $AsCl_3$ (10 g, 55.2 mmol) in THF (10 mL) was cooled to −10 °C. Then a THF solution (8.5 mL) containing **2** (4.0 mmol) was added dropwise. The resulting dark brown reaction mixture was warmed to room temperature. After evaporation of the reaction mixture under reduced pressure, the residue was extracted three times with pentane (50 mL). Several crystallizations did not furnish pure **4**. Upon cooling, brown and yellow crystals were formed; the yellow crystals became brown upon standing, even at −20 °C. **4**: NMR (see also Tables 1 and 2) (C_6D_6) $\delta(^{13}C\{^1H\})$ 21.7 (ddq, $\{^3J(CH) = 5.3\}$, $\{^1J(CH) = 127.0\}$, 4-CH_3), 23.0 (ddq, $\{^3J(CH) = 6.3\}$, $\{^1J(CH) = 127.3\}$, 5-CH_3), 154.1 (ddq, $\{^1J(CH) = 154.9\}$, $\{^3J(CH) = 5.4\}$, C6), quaternary carbon atoms were not detected; $\delta(^{31}P\{^1H\})$ 198.6. HRMS calcd for $C_7H_8As^{35}Cl_2P$ 267.8957, found 267.896; MS (EI) *m/e* 268 ($[M]^+$, 62), 233 ($[M - Cl]^+$, 100), 198 ($[M - 2Cl]^+$, 10), 123 ($[M - AsCl_2]^+$, 65).

(17) Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 793.

[η^1-2-(Dichloroarsino)-4,5-dimethylphosphinine]pentacarbonyltungsten (5). A solution of $AsCl_3$ (1.3 g, 7.2 mmol) in THF (5 mL) was cooled to −40 °C. Then a THF solution (3 mL) containing **3** (1.2 mmol) was added dropwise. The resulting black reaction mixture was allowed to warm to room temperature. Concentration to 3 mL was followed by mixing with pentane (100 mL). A large amount of dark brown precipitate was formed. Separation of the supernatant and cooling to −70 °C led to the formation of orange crystals, which consisted of three components with $\delta(^{31}P\{^1H\})$ of 165.6, 159.5 and 154.8 ppm in the following ratio 146.2:53.0:17.5 ($^{31}P\{^1H\}$). It is assumed that the most abundant component is **5**. **5**: NMR (see also Tables 1 and 2) (C_6D_6) $\delta(^{13}C)$ 194.2 (d, ^2J(PC) = 8.8, ^1J(WC) = 124.5, CO (cis)), 197.5 (d, ^2J(PC) = 29.6, CO (trans)); $\delta(^{31}P\{^1H\})$ 165.4 (^1J(PW) = 268.4). HRMS calcd for $C_{12}H_8As^{35}Cl_2O_5P^{182}W$ 589.8185, found 589.819, MS (EI) *m/e* 594 ([M]$^+$, 22), 566 ([M − CO]$^+$, 14), 485 ([M − 4CO]$^+$, 10), 454 ([M − 5CO]$^+$, 100), impurities (^{31}P NMR, vide supra); **7** 448 ([M]$^+$), 392 ([M − 2CO]$^+$), 364 ([M − 3CO]$^+$), 336 ([M − 4CO]$^+$) ((η^1-3,4-dimethylphosphinine)pentacarbonyltungsten); **6** 686 ([M]$^+$), 658 ([M]$^+$ − CO), 600 ([M]$^+$ − 3CO) ([η^1-2-(chloroiodoarsino)-4,5-dimethylphosphinine]pentacarbonyltungsten).

2-(Dichlorophosphino)-4,5-dimethylphosphinine (8). A solution of PCl_3 (14 mL, 0.16 mol) in THF (10 mL) was cooled to −60 °C. Then a THF solution (20 mL) containing **2** (10 mmol) was added dropwise while stirring. A red precipitate was formed, and after completion of the addition, the reaction mixture was allowed to warm to room temperature. Removal of volatile components under reduced pressure was followed by two extractions of the residue with pentane (100 mL). Several crystallizations did not furnish pure **8**. The formation of **10** during the reaction was a complicating factor as well as the fact that **8** decomposed slowly at room temperature. **8**: NMR (see also Tables 1 and 2) (C_6D_6) $\delta(^1H)$ 8.01 (dd, ^4J(PH) = 6.2, 1H, H6), 8.12 (dd, ^3J(PH) = 12.7, 1H, H3); $\delta(^{13}C\{^1H\})$ 21.7 (dddq, {^3J(CH) = 5.4}, {^4J(CH) = 0.8}, {^1J(CH) = 127.0}, 4-CH_3), 23.1 (ddq, ^5J(PC) = 1.8, {^1J(CH) = 127.2}, 5-CH_3), 139.3 (dddq, ^2J(PC) = 24.4, {^1J(CH) = 162.8}, {^3J(CH) = 5.5}, C3), 140.1 (dd, ^3J(PC) = 6.0, C4), 154.3 (dddq, ^3J(PC) = 20.6, {^1J(CH) = 154.9}, {^3J(CH) = 5.0}, C6), 167.0 (td, ^1J(PC) = 63.0, {^3J(CH) = 9.1}, C2); $\delta(^{31}P\{^1H\})$ 165.3 (P(Cl_2)), 204.8 (P(ar)) (^2J(PP) = 242.4). HRMS calcd for $C_7H_8{}^{35}Cl_2P_2$ 223.9478, found 223.947; MS (EI) *m/e* 224 ([M]$^+$, 100), 189 ([M − Cl]$^+$, 43).

[η^1-2-(Dichlorophosphino)-4,5-dimethylphosphinine]pentacarbonyltungsten (11). A solution of PCl_3 (excess, freshly distilled) in THF (3 mL) was cooled to −60 °C. Then a THF solution (2 mL) containing **3** (0.70 mmol) was added dropwise. After the addition of **3**, a brown precipitate was formed and the reaction mixture was warmed to room temperature. **11**: NMR (THF) $\delta(^{31}P\{^1H\})$ 174.2 (P(ar)), 158.4 (P(Cl_2)), ^2J(PP) = 278.1 ,^1J(PW) = 273.8.

2-(Triphenylstannyl)-4,5-dimethylphosphinine (13). The organozinc reagent **1** was prepared from zinc powder (0.68 g, 10.4 mmol) and **10** (1.23 g, 4.92 mmol) in DMF (7.5 mL) by stirring for 18 h at room temperature. This solution was added dropwise over 5 min to a solution of $ClSnPh_3$ (1.89 g, 4.9 mmol) in DMF (2 mL). After stirring for 15 min, a white precipitate was formed. The solvent was removed under vacuum, and the residue was extracted with toluene (40 mL) and filtered. After evaporation of the filtrate under reduced pressure, the residue was recrystallized several times from pentane to furnish pure **13** as colorless crystals (mp 122−3 °C) in a yield of 37% (0.86 g, 1.82 mmol) relative to **10**. **13**: NMR (see also Tables 1 and 2) (C_6D_6) $\delta(^1H)$ 7.05−7.35 (m, 9H, *m*-, *p*-$SnPh_3$), 7.75−7.85 (m, 6H, *o*-$SnPh_3$), 8.13 (d, ^3J(SnH) = 69.6, 1H, H3), 8.48 (d, ^4J(SnH) = 26.8, 1H, H6); $\delta(^{13}C\{^1H\})$ 22.0 (dddq, {^3J(CH) = 5.4}, {^4J(CH) = 0.7}, {^1J(CH) = 127.4}, 4-CH_3), 23.3 (dddq, {^3J(CH) = 6.5}, {^4J(CH6) = 0.7}, {^1J(CH) = 126.7}, 5-CH_3), 129.1 (d, ^3J(SnC) = 52.3, {^1J(CH) = 154.9}, $SnPh_3$ *m*-C), 129.5 (dt, ^4J(SnC) = 11.6, {^1J(CH) = 158.9}, {^3J(CH) = 14.1}, $SnPh_3$ *p*-C), 137.8 (dd, ^4J(PC) = 1.2, ^2J(SnC) = 37.1, {^1J(CH) = 159.0}, $SnPh_3$ *o*-C), 138.6 (d, ^3J(PC) = 3.4, $SnPh_3$ *ipso*-C), 144.9 (ddq, ^2J(SnC) = 14.7, {^1J(CH) = 155.3}, {^3J(CH) = 5.2}, C3), 156.7 (ddq, $^3J(^{119}SnC)$ = 56.3, $^3J(^{117}SnC)$ = 55.0, {^1J(CH) = 152.0}, {^3J(CH) = 5.2}, C6); $\delta(^{31}P\{^1H\})$ 222.0 ($^2J(P^{117}Sn)$ = 303.0, $^2J(P^{119}Sn)$ = 317.3); $\delta(^{119}Sn)$ −125.4. HRMS calcd for $C_{25}H_{23}P^{120}Sn$ 474.0562, found 474.0588; MS (EI) *m/e* 474 ([M]$^+$, 29), 397 ([M − Ph]$^+$, 31), 351 ([M − C_7H_8P]$^+$, 100). Anal. Calcd for $C_{25}H_{23}$-PSn: C, 63.47; H, 4.90; P, 6.55; Sn, 25.09. Found: C, 62.57; H, 4.93; P, 5.99; Sn, 24.1.

Bis(4,5-dimethylphosphininyl-κC^2)dimethyltin (14) and bis((4,5-dimethylphosphininyl-1κP, 2κC^2)pentacarbonyltungsten)dimethyltin (16). Synthesis of 14. To a solution of freshly sublimed $Cl_2Sn(CH_3)_2$ (0.53 g, 2.42 mmol) in THF (3 mL), 6.5 mL of a DMF solution containing 4.8 mmol of **1**, prepared as described above, was added dropwise while stirring. After 3.5 h of stirring at room temperature, the solution was evaporated under vacuum. The residue was extracted three times with toluene (25 mL); after filtration, the filtrate was evaporated under vacuum. Extraction of the residue with pentane was followed by crystallization by cooling the extract to −70 °C. After several futile attempts to obtain pure crystals, it became evident that **14** was too unstable to be isolated in pure form. The initially colorless crystals turned yellowish rather rapidly upon standing. **14**: NMR (see also Tables 1 and 2) (C_6D_6) $\delta(^1H)$ 0.74 (s, $^2J(^{119}SnH)$ = 55.9, $^2J(^{117}SnH)$ = 53.6, 6H, $SnMe_2$), 8.10 (d, ^3J(SnH) = 66.2, 1H, H3), 8.45 (d, ^4J(SnH) = 24.0, 1H, H6); $\delta(^{13}C\{^1H\})$ −8.1 (tq, ^3J(PC) = 4.9, $^1J(^{119}SnC)$ = 364.9, $^1J(^{117}SnC)$ = 355.0, {^1J(CH) = 130.2}, $SnMe_2$), 22.1 (dq, {^3J(CH) = 4.8}, {^1J(CH) = 126.5}, 4-CH_3), 23.4 (ddq, {^3J(CH) = 6.3}, {^4J(CH) = 2.5}, {^1J(CH) = 126.6}, 5-CH_3), 138.0 (d, ^3J(PC) = 25.6, C4), 143.8 (AXX′ {ddq}, {^1J(CH) = 153.9}, {^3J(CH) = 5.2}, C3), 156.5 (ddq, ^3J(SnC) = 54.3, {^1J(CH) = 151.5}, {^3J(CH) = 4.9}, C6), 167.7 (dd, ^3J(PC) = 4.4, C2); $\delta(^{31}P\{^1H\})$ 218.5 ($^2J(P^{119}Sn)$ = 330.8, $^2J(P^{117}Sn)$ = 316.1). HRMS calcd for $C_{16}H_{22}P_2{}^{120}Sn$ 396.022, found 396.023; MS (EI) *m/e* 396 ([M]$^+$, 5), 381 ([M − CH_3]$^+$, 24), 366 ([M − 2CH_3]$^+$, 7), 273 ([M − C_7H_8P]$^+$, 13).

Synthesis of 16. All crude **14** (vide supra) was combined and dissolved in THF (10 mL) after which **15** (1.0 g, 2.7 mmol) was added. This mixture was stirred at room temperature for 30 h and evaporated; the residue was extracted with pentane (80 mL). Crystallization of the pentane extract furnished pure **16** as yellow crystals (mp 157 °C) in a yield of 7% (0.17 g, 0.16 mmol) relative to **10**. **16**: NMR (see also Tables 1 and 2) (C_6D_6) $\delta(^1H)$ 0.88 (s, $^2J(^{119}SnH)$ = 56.9, $^2J(^{117}SnH)$ = 54.5, 6H, $SnMe_2$), 7.75 (d, ^2J(SnH) = 66.4, 1H, H3), 8.23 (d, ^4J(SnH) = 23.9, 1H, H6); $\delta(^{13}C\{^1H\})$ −4.6 (tq, ^3J(PC) = 1.8, {^1J(CH) = 130.8}, $SnMe_2$), 21.7 (ddq, {^3J(CH) = 4.6}, {^1J(CH) = 126.9}, 4-CH_3), 22.9 (dq, {^1J(CH) = 126.3}, 5-CH_3), 136.6 (d, ^3J(SnC) = 43.9, C4), 147.5 (ddq, ^2J(SnC) = 11.1, {^1J(CH) = 156.1}, {^3J(CH) = 5.9}, C3), 148.5 (d, ^4J(SnC) = 10.7, C5), 154.0 (dd, ^3J(SnC) = 38.6, {^1J(CH) = 157.9}, C6), 161.3 (dd, ^3J(PC) = 4.4, C2), 195.9 (d, ^2J(PC) = 9.3, ^1J(WC) = 124.8, CO (cis)), 198.2 (d, ^2J(PC) = 28.1, CO (trans)); $\delta(^{31}P\{^1H\})$ 176.8 (^1J(PW) = 262.8, $^2J(P^{119}Sn)$ = 213.5, $^2J(P^{117}Sn)$ = 205.2). HRMS calcd for $C_{26}H_{22}O_{10}P_2{}^{118}Sn^{184}W_2$ 1041.8726, found 1041.874; MS (EI) *m/e* 1042 ([M]$^+$, 1), 690 ([M − W(CO)6]$^+$, 3), 634 ([M − $W(CO)_6$ − 2CO]$^+$, 7), 578 ([M − $W(CO)_6$ − 4CO]$^+$, 13). Anal. Calcd for $C_{26}H_{22}O_{10}P_2SnW_2$: C, 29.95; H, 2.13; P, 5.94. Found: C, 30.37; H, 2.29; P, 5.91.

4,5-Dimethyl-3′-(trimethylsiloxy)-1′,4′,5′,6′-tetrahydro-2-phosphabiphenyl (19). A solution of **2** (6.08 mmol) and 2-cyclohexen-1-one (1.76 g, 18.3 mmol) in THF (13 mL) was cooled to −90 °C. Then a light green THF solution (8 mL) containing CuCN·2LiBr (prepared from CuCN (0.66 g, 7.37 mmol) and LiBr (1.52 g, 17.5 mmol)) and $ClSi(CH_3)_3$ (2.4 g, 22 mmol) was added over 30 min. During 3 h the temperature was maintained between −80 and −100 °C. Then the black reaction mixture was allowed to warm to room temperature. Concentration to 15 mL was followed by extraction with pentane (75 mL). The upper layer was removed, and THF (8

mL) was added to the lower layer. Extraction of the THF layer was carried out with pentane (75 mL), and the extraction procedure was repeated once more. The combined extracts were concentrated to 50 mL and cooled to −70 °C. Some dark brown oil was formed which did not contain phosphorus compounds as evidenced by a ^{31}P NMR spectrum. Addition of pentane to the upper layer lead to separation of salts as a dark oil. This cycle of operations was continued until a salt-free pentane extract containing **9** and **19** was obtained. The resulting extract (5 mL) was evaporated under vacuum to give nearly pure **19** as a brown oil in a yield of 20% (0.35 g, 1.20 mmol) relative to **10**. **19**: NMR (see also Tables 1 and 2) (C_6D_6) $\delta(^1H)$ 0.27 (s, 9H, 3′-OSi(CH_3)$_3$), 1.35 (m, 1H, H4′), 1.50 (m, 1H, H6′), 1.65 (m, 1H, H5′), 1.90 (m, 1H, H6′), 2.10 (m, 1H, H4′), 2.10 (m, 1H, H5′), 3.85 (m, 1H, H1′), 5.24 (m, 1H, H2′); $\delta(^{13}C\{^1H\})$ 0.7 (q, $\{^1J(CH) = 118.6\}$, 3′-OSi(CH_3)$_3$), 21.9 (t, $\{^1J(CH) = 125.3\}$, C5′), 22.4 (ddq, $\{^3J(CH) = 5.7\}$, $\{^1J(CH) = 126.3\}$, 5-CH_3), 22.9 (ddq, $\{^3J(CH) = 6.5\}$, $\{^1J(CH) = 126.3\}$, 4-CH_3), 30.3 (t, $\{^1J(CH) = 125.5\}$, C4′), 35.4 (dt, $^3J(PC) = 6.3$, $\{^1J(CH) = 132.6\}$, C6′), 45.0 (dd, $^2J(PC) = 28.0$, $\{^1J(CH) = 128.1\}$, C1′), 136.3 (ddq, $\{^1J(CH) = 150.7\}$, $\{^3J(CH) = 5.3\}$, C6), 154.8 (ddq, $\{^1J(CH) = 151.0\}$, $\{^3J(CH) = 4.9\}$, C3); $\delta(^{31}P\{^1H\})$ 190.2. HRMS calcd for $C_{16}H_{25}OP^{28}Si$ 292.1412, found 292.141; MS (EI) *m/e* 292 ($[M]^+$, 27), 277 ($[M - CH_3]^+$, 20), 202 ($[M - HOSi(CH_3)_3]^+$, 2), 169 ($[M - C_7H_8P]^+$, 100). Anal. Calcd for $C_{16}H_{25}OPSi$: C, 65.72; H, 8.62. Found: C, 67.80; H, 9.08.

(η^1-2-Cupri-4,5-dimethylphosphinine)pentacarbonyltungsten (20). Synthesis of 20 via 3. A solution of CuCN·2LiCl in THF (3 mL), prepared from LiCl (0.20 g, 4.65 mmol) and CuCN (0.06 g, 0.67 mmol) was cooled to −60 °C. Then a THF solution (2 mL) containing **3** (0.70 mmol) was added dropwise. After addition of **3**, the resulting light brown solution was warmed to room temperature. Decomposition of **20** at room temperature was complete within 6 h; in the ^{31}P NMR spectrum, two new signals appeared around 55 ppm and one at 37 ppm. **20**: NMR (THF) $\delta(^{31}P\{^1H\})$ 171.2 ($^1J(PW) = 249.9$).

Synthesis of 20 via 12.[8] The highly reactive Cu(0) was prepared by dropwise addition of a solution of CuCN·2LiBr (1.0 mmol) in THF (1 mL) to lithium naphthalenide (1.1 mmol) in THF (2 mL) at −100 °C. After 5 min stirring at −100 °C, a solution of **12** (0.25 mmol) in THF (0.6 mL) was added dropwise. Then the reaction mixture was warmed slowly to room temperature. Subsequent measurement of a ^{31}P NMR spectrum showed the presence of **20**, **7**, and a component with $\delta(^{31}P)$ 227 ppm, in a ratio of 10.6:1:2.6. **20**: ($\delta(^{31}P)$ 171 ppm, $^1J(PW) = 244$). The decomposition of **20**, obtained from **3** or **12**, proceeded in a similar fashion: two signals appeared around 55 ppm; but the signal at 37 ppm did not appear.

2-Argentio-4,5-dimethylphosphinine (21″). A solution of **2** was prepared from **10** (1.35 g, 5.4 mmol), TMEDA (1.37 g, 11.8 mmol), and zinc powder (0.7 g, 10.7 mmol) in THF (5 mL). Of this solution, 0.9 mL was added dropwise to a solution of AgBr·2LiBr (prepared from AgBr (0.19 g, 1.0 mmol) and LiBr (0.19 g, 2.2 mmol) in THF (3 mL)), which was cooled −40 °C. The reaction mixture became red and was allowed to slowly warm to room temperature. At room temperature, a grey precipitate formed slowly. NMR measurements showed the presence of **21″**. After that, the NMR sample was stored at 4 °C. After 5 days, **21″** was completely decomposed with concomitant formation of 3,4-dimethylphosphinine ($\delta(^{31}P\{^1H\})$ 191) and a grey precipitate. **21″**: NMR (see also Table 2) (THF + C_6D_6) $\delta(^{13}C\{^1H\})$ 46.8 (s, NCH_3), 57.6 (s, NCH_2); $\delta(^{31}P\{^1H\})$ 194.1; TMEDA (THF + C_6D_6): $\delta(^{13}C)$ 45.5 (s, NCH_3), 58.1 (s, NCH_2).

Bis(4,5-dimethylphosphininyl-κC^2)mercury (22). Synthesis via 1. To 1 mL of a DMF solution containing 0.9 mmol of **1** was added $HgCl_2$ (0.10 g, 0.37 mmol); a pale white precipitate was formed immediately. After evaporation of the solution under vacuum, the residue was extracted with toluene (10 mL). Evaporation of the extract under vacuum was followed by extraction of the residue with C_6D_6 (1 mL). As decomposition occurred within several hours, **22** could not be isolated in pure form. In the ^{1}H NMR spectrum of **22**, signals originating from DMF were present. Relative to a reference sample of DMF in C_6D_6, the amide proton was shifted 0.26 ppm downfield and one methyl group was shifted 0.16 ppm upfield; the other methyl group did not show any shift. **22**: NMR (see also Table 1) (C_6D_6) $\delta(^1H)$ 1.95 (s, 3H, NCH_3), 2.25 (s, 3H, NCH_3), 7.95 (s, 1H, CHO); $\delta(^{31}P\{^1H\})$ 213.1 ($^2J(PHg) = 799.7$). Reference spectrum of DMF (C_6D_6) $\delta(^1H)$ 1.95 (s, 3H, NCH_3), 2.41 (s, 3H, NCH_3), 7.69 (s, 1H, CHO).

Synthesis via 2. A solution of **2** (1.24 mmol) and TMEDA (0.20 g, 1.72 mmol) in THF (10 mL) was cooled to −60 °C. Then $HgCl_2$ (0.18 g, 0.66 mmol) was added, after which the dark red solution was warmed slowly to room temperature, during which a brown precipitate was formed. Addition of pentane (10 mL) led to the formation of more voluminous precipitate. The supernatant was separated and cooled, and the resulting light brown crystals, contaminated with some grey powder, were separated and dried. As MS indicated the presence of zinc salts and NMR spectroscopy indicated slow decomposition at room temperature, **22** could not be isolated in pure form. **22**: NMR (see also Tables 1 and 2) ($CDCl_3$) $\delta(^1H)$ 7.89 (d, $^3J(HgH) = 143.1$, 1H, H3), 8.67 (d, $^4J(HgH) = 43.6$, 1H, H6), 2.63 (s, 12H, NCH_3), 2.74 (s, 4H, NCH_2), TMEDA:**22** = 1.46:1; $\delta(^{13}C)$ 48.3 (s, NCH_3), 56.8 (s, NCH_2), 194.7 (dd, $^3J(PC) = 7.2$, C2); $\delta(^{31}P\{^1H\})$ 212.8 ($^2J(PHg) = 786.1$). Reference spectrum of TMEDA ($CDCl_3$) $\delta(^1H)$ 2.23 (s, 12H, NCH_3), 2.38 (s, 4H, NCH_2); $\delta(^{13}C)$ 45.6 (s, NCH_3), 57.4 (s, NCH_2).

Bis-[(4,5-dimethylphosphininyl-1κP,2κC^2)pentacarbonyltungsten]mercury (23). A solution of **3** (3.52 mmol) in THF (10 mL) was cooled to 0 °C. Then a solution of $HgCl_2$ (0.48 g, 1.77 mmol) in THF (2 mL) was added quickly while stirring. A large amount of yellow precipitate was formed in the dark red solution. After addition of pentane, the reaction mixture was filtered and washed twice with THF (30 mL) and finally with pentane (30 mL) and dried. This procedure furnished pure **23** (mp 192 °C dec) as a very light yellow green powder in a yield of 50% (0.97 g, 0.89 mmol) relative to **10**. **23**: NMR (see also Tables 1 and 2) (THF-d_8) $\delta(^1H)$ 7.95 (d, $^3J(HgH) = 147.5$, 1H, H3), 8.52 (d, $^4J(HgH) = 48.0$, 1H, H6); $\delta(^{13}C\{^1H\})$ 195.2 (d, $^2J(PC) = 9.4$, CO (cis)); $\delta(^{31}P\{^1H\})$ 175.1 ($^2J(PHg) = 627.7$, $^1J(PW) = 261.6$). HRMS calcd for $C_{24}H_{16}{}^{202}HgO_{10}P_2{}^{182}W^{184}W$ 1093.8918, found 1093.890; MS (EI) *m/e* 1094 ($[M]^+$, 18), 726 ($[M - W(CO)_6 - CH_3 - H - CO]^+$, 13), 698 ($[M - W(CO)_6 - CH_3 - H - 2CO]^+$, 17), 670 ($[M - W(CO)_6 - CH_3 - H - 3CO]^+$, 29). Anal. Calcd for $C_{24}H_{16}HgO_{10}P_2W_2$: C, 26.33; H, 1.47; Hg, 18.32; P, 5.66. Found C, 25.70; H, 1.54; Hg, 19.4; P, 5.42.

OM9506936