Synthesis and Reactivity of 2-Iodophosphinines

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The synthesis of 2-iodophosphinines **5** (**a**, parent compound; **b**, 4,5-dimethyl derivative) and of their pentacarbonyltungsten complexes **7** is described starting from dichloro(diiodomethyl)phosphine (**2**), which was prepared via alkylation of phosphorus trichloride with (diiodomethyl)magnesium chloride (**1**). The halogen−metal exchange reactions of **5a**/**b** and **7a**/**b** are reported: the lithiation reactions of **5a**/**b** with *n*-BuLi were not successful. In contrast, the complexes **7a**/**b** were converted to the corresponding lithium derivatives **11a**/**b** with *n*-BuLi in THF at −100 °C. Derivatization of **11a**/**b** with triphenyltin chloride furnished **13a**/**b**, respectively. The reaction of **5b** with magnesium in THF at room temperature led to the formation of 3,4-dimethylphosphinine (**18**) (41.5%), 4,4′,5,5′-tetramethyl-2,2′-biphosphinine (**16**) (1.3%), and 2-(iodomagnesio)-4,5-dimethylphosphinine (**17**) (19.2%); 37% of the starting material had decomposed. In a reaction with zinc, **5b** gave the organozinc derivatives **20** or **21** in THF/TMEDA or DMF, respectively. The same zinc insertion procedures were applied to **7b** but did not furnish the pentacarbonyltungsten complexes **22** or **24** in a clean fashion. However, **22** could be prepared via complexation of **20** with (acetonitrile)-pentacarbonyltungsten (**6**).

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 non-phosphaaromatic prcursors.[2] In principle, preparation of a new phosphinine via chemical modification of a halophosphinine might be an interesting approach to obtain a variety of functionalized phosphinines. Along this line, Mathey *et al.* investigated the chemistry of 2-chloro- and 2-bromophosphinines.[3] As we were interested in phosphinines functionalized at the 2-position, we focused our attention on the synthesis and reactivity of 2-iodo derivatives in the hope that the enhanced reactivity of the carbon−iodine bond would open new perspectives for investigations on 2-halophosphinines in general. In preliminary communications[4] we reported on the synthesis of 2-iodophosphinines and on several exploratory results concerning their reactivity. In this paper we wish to report the synthesis of 2-iodophosphinines **5a**/**b** and their pentacarbonyltungsten complexes **7a**/**b** with full experimental details. Furthermore, metalation reactions of these compounds with *n*-butyllithium, magnesium, and zinc are described.

While halogen−metal exchange with organolithium reagents and the preparation of Grignard reagents is well-known, direct zinc insertion into C−X bonds is less common. However, recently, Knochel provided some important contributions to the preparation of organozinc compounds.[5] One of these[5a] concerns the preparation of arylzinc iodides in DMF or DMAC (dimethylacetamide) via direct zinc insertion into an aryl−iodine bond. Another zinc insertion into an sp^2-hybridized C−X bond was reported by Jiang and Xu.[6] With 2-bromotrifluoropropene as the substrate, they investigated a variety of solvents (Et_2O, THF, DME, and DMF) and a zinc/silver couple in the presence or absence of TMEDA. It was found that in the presence of TMEDA (1 equiv) in THF, DME, or Et_2O, the corresponding organozinc derivative was obtained in high yield while poor results were obtained in DMF.

Results and Discussion

Iodophosphinines. The synthesis of 2-iodophosphinines and their pentacarbonyltungsten complexes was achieved by the Diels−Alder approach developed by Mathey for the corresponding chlorine and bromine derivatives[3a] and is outlined in Scheme 1.

The precursor **2** was prepared by alkylation of phosphorus trichloride with the magnesium carbenoid **1**. The freshly prepared solution of **1**[7] was frozen in liquid nitrogen at −196 °C. Then a Schlenk tube containing

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(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, Germany, 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.

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(6) Jiang, B.; Xu, Y. *J. Org. Chem.* **1991**, *56*, 7336.

(7) Seyferth, D.; Lambert, R. L. *J. Organomet. Chem.* **1973**, *54*, 123.

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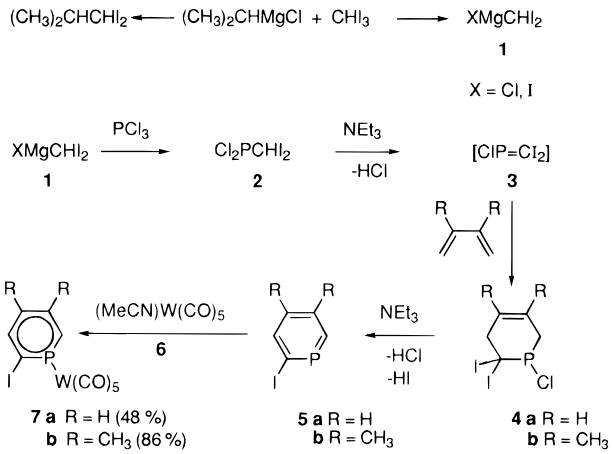
Scheme 1



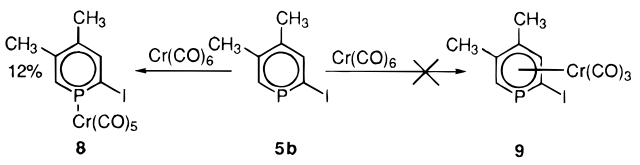
freshly distilled, frozen (−196 °C) phosphorus trichloride (13 equiv) was attached up side down on top of the frozen solution of **1**. The Schlenk tube was allowed to warm such that phosphorus trichloride was dropping at its melting point (−112 °C) down on top of the frozen solution of **1**. After the phosphorus trichloride had been added, the cooling bath was removed and the reaction mixture warmed to −100 °C. At this temperature, the mixture began to melt and the reaction could occur in the presence of a large excess of phosphorus trichloride, which was expected to suppress di- and trialkylation. In spite of its successful synthesis from **1**, **2** ($\delta(^{31}P)$ 155.2 ppm) could not be purified by distillation or crystallization. Therefore, the subsequent Diels−Alder reactions with a 1,3-butadiene were carried out with freshly prepared crude **2**, which, according to ^{31}P NMR spectroscopy, was approximately 70% pure.

The Diels−Alder reactions were carried out at relatively low temperatures: −5 °C for 1,3-butadiene (**a** series, 23 equiv) and 0 °C for 2,3-dimethylbutadiene (**b** series, 20 equiv). A large excess of triethylamine (**a**, 11 equiv; **b**, 17 equiv) was added to a solution of **2** in the diene to generate the unstable phosphaalkene **3** and to aromatize its primary Diels−Alder adducts **4**; to achieve this, the reaction mixture was allowed to warm slowly to room temperature.

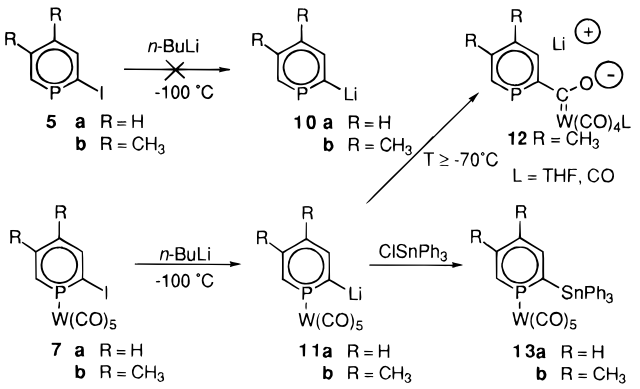
The aromatization of **4** was monitored by ^{31}P NMR spectroscopy. The aromatization of **4a** required less than 16 h. On the other hand, 55 h stirring at room temperature was necessary to convert **4b** ($\delta(^{31}P)$ 94 ppm) to **5b**. The 2-iodophosphinines were isolated by distillation under high vacuum in a yield of 32% (**5b**, yellow crystals ($\delta(^{31}P)$ 216 ppm)) and 10% (**5a**, yellow liquid ($\delta(^{31}P)$ 233 ppm)) relative to iodoform, the precursor of **1** (Scheme 1).[7] Whereas **5b** was isolated in pure form, **5a** was slightly contaminated with 1,1-diiodoisobutane (5−10%) which is formed as a byproduct, presumably in the preparation of **1** from iodoform and isopropylmagnesium chloride (Scheme 1). Distillative separation of 1,1-diiodoisobutane was easy for **5b** but impossible in the case of **5a**.

Phosphinines **5** were fully characterized by NMR, MS, and elemental analysis. The NMR assignments were supported by 2D NMR techniques. While HH COSY, CH COSY, COLOC, and 1D NOE did not distinguish between C4 and C5 in **5b**, INADEQUATE solved this problem conveniently. The ^1J(CC) values of the phosphinine ring lie in the range 55.3−58.7 Hz, which is close to the value of benzene[8] (57.0 Hz) and confirms the electronic delocalization within the aromatic ring. Furthermore, the ^1J(CC) values involving the methyl groups (42.6−43.67 Hz) are very close to those in *o*-xylene[8] (44.2 Hz). The pentacarbonyltungsten complexes **7a** ($\delta(^{31}P)$ 202 ppm, $^1J(PW) = 286$ Hz) and **7b** ($\delta(^{31}P)$ 185 ppm, $^1J(PW) = 280.4$ Hz) were prepared in moderate to high yield by reacting **5a**,**b** with (acetonitrile)pentacarbonyltungsten[9] (**6**) in THF at room temperature (**7a**) or 45−50 °C (**7b**) (Scheme 1). In these reactions, a small excess of **6** (about 10%) was necessary to drive the complexation to completion.

Scheme 2



Scheme 3



In the reactivity studies, the attention was focused on the dimethyl derivatives **5b** and **7b**, as **5b** could be obtained in pure form and in higher yield. Furthermore, its synthesis is less complicated than that of **5a** because of the easy handling of 2,3-dimethyl-1,3-butadiene compared with 1,3-butadiene.

Attempts to prepare the η^6 complex **9** by heating **5b** for several hours under reflux in di-*n*-butyl ether with hexacarbonylchromium analogous to the procedures of Nöth[10] failed; besides decomposition products of **5b**, only the η^1 complex **8** ($\delta(^{31}P)$ 231 ppm) was formed (Scheme 2). Apart from decomposition, the lack of steric hindrance at positions 2 and 6 of the phosphinine ring probably is an important factor for this failure.[11] Compound **8** was isolated in low yield (12%) and was fully characterized by NMR and MS spectroscopy.

Organolithium Derivatives. Toward 1.6 M *n*-BuLi, there are some interesting differences in behavior between uncoordinated 2-iodophosphinines **5** and their pentacarbonyltungsten complexes **7**. As outlined in Scheme 3, the lithiation of uncoordinated 2-iodophosphinines did not occur, whereas the pentacarbonyltungsten complexes showed the expected iodine−lithium exchange. Reaction of 1.6 M *n*-BuLi (1 equiv) with **5a**/**b** in THF was performed at −100 °C. After 0.5 h of

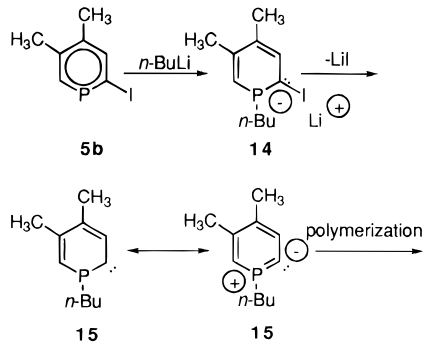
(8) Wray, V. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *13*, 177.
(9) Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 793.
(10) Deberitz, J.; Nöth, H. *Chem. Ber.* **1970**, *103*, 2541.
(11) Nainan, K. C.; Sears, C. T. *J. Organomet. Chem.* **1978**, *148*, C31.

stirring of the black reaction mixtures at temperature below −80 °C, a quench reaction with $ClSnR'_3$ (R′ = Ph (**5b**), R′ = CH_3 (**5a**)) was carried out. After warming of the samples to room temperature, ^{31}P NMR spectroscopy indicated complete decomposition in the case of **5b** and the formation of many non-phosphaaromatic compounds with a poor signal to noise ratio in the case of **5a**. In the latter case, the experiment was not conclusive with respect to the lithiation of **5a**, because of the presence of 1,1-diiodoisobutane.

The lithiation of the pentacarbonyltungsten complexes was successful, and the organolithium phosphinines **11a**/**b** could be detected by low-temperature ^{31}P NMR spectroscopy. The thermal decomposition of **11a**/**b** was followed as a function of temperature; **11b** ($\delta(^{31}P)$ 163.4 ppm, $^1J(PW) = 239.8$ Hz) turned out to decompose at −70 °C. In the ^{31}P NMR spectra, signals appeared between 0 and −100 ppm and around 240 ppm. At room temperature the most important signals were located at 242 and 7 ppm with a rather unsatisfactory signal to noise ratio. The signal at 242 ppm did not show tungsten satellites so this compound might be the Fischer carbene **12** (Scheme 3), which could be formed by an intramolecular attack of the C−Li bond on CO. Such intramolecular reaction would result in a strained four-membered ring system, which opens by disruption of the coordination between phosphorus and tungsten; it is reasonable to assume that the resulting vacant coordination site at tungsten is filled by a Lewis base such as THF or CO to furnish an 18 electron species as indicated. The spectroscopic detection of **11a** was more difficult as its formation was not selective and the thermal stability rather low. The first recorded spectrum at −85 °C showed the presence of **11a** ($\delta(^{31}P)$ 176.9 ppm, $^1J(PW) = 235.2$ Hz) and many signals in the region of 8 to −52 ppm. The spectrum recorded at −80 °C showed already substantial decomposition, thus indicating that methyl groups at the 4- and 5-positions lead to increased stability of (organometallic) phosphinine derivatives. Both organolithium derivatives were quenched with triphenyltin chloride at −90 or −100 °C, and the organotin derivatives **13a**/**b** were isolated in pure form and were fully characterized. The yield of **13b** was moderate (48%), but **13a** was obtained in a rather disappointing yield (4%). The steric shielding of the 2-position of the phosphinine by the $W(CO)_5$ moiety might be responsible for a rather slow reaction of triphenyltin chloride. The competition between decomposition of **11a**/**b** on the one hand and nucleophilic substitution at tin on the other is more detrimental for **11a** than for **11b**. Mathey *et al.* encountered similar unexpected difficulties in quench reactions of a molybdenum-coordinated 2-lithiophosphinine.[3d] Apparently, substituents can have a substantial influence on the effectiveness with which an organolithiophosphinine is derivatized. In addition, the purification of **13a** turned out to be difficult; many crystallizations were required before it was isolated in pure form.

The question why halogen−lithium exchange is not successful in the case of **5a**/**b**, whereas for the pentacarbonyltungsten complexes, notably **7b**, it is achieved rather easily, is difficult to answer. Mathey *et al.* suggested that a strong stabilizing interaction between the phosphaaromatic system and the halogen (Cl, Br) could account for the inertness of free 2-halophosphinines[3b] toward lithiation at the 2-position;[3c] it was suggested that this stabilization is less pronounced in the pentacarbonyltungsten complex in which the aromaticity of the phosphinine ring is somewhat reduced.[12] We propose that, in 2-iodophosphinines **5a**/**b**, reaction with the organolithium reagents results in a competition between nucleophilic attack at phosphorus and halogen−metal exchange. Due to the interaction between the 2-halogen substituent and the phosphinine ring, which seems operational in 2-iodophosphinines, too, the reaction is dominated by nucleophilic attack at phosphorus to give **14** (Scheme 4).[13] Possibly, decomposition proceeds via cleavage of the C−I bond, which leads to the formation of **15**, a phosphinin-2-ylidene derivative which has been shown to be a local minimum by *ab initio* calculations.[14] Its polymerization may be the cause of decomposition; Scheme 4 shows only this decomposition pathway, but others are conceivable. Apparently, nucleophilic attack at phosphorus is less competitive in **7**, probably for steric reasons.

Scheme 4



In conclusion, the halogen−lithium exchange of neither **5a**/**b** nor the 2-bromo- or 2-chlorophosphinines[3b] could be achieved. In contrast, the pentacarbonyltungsten complexes **7a**/**b** are easily converted to the corresponding 2-lithiophosphinines **11a**/**b** by *n*-BuLi. The pentacarbonyltungsten complex of a 2-bromophosphinine has been reported to undergo halogen−metal exchange in reaction with phenyllithium;[3c] so in this respect our 2-iodophosphinines do not exhibit unique behavior.

Organomagnesium Derivatives. In contrast to the iodine−lithium exchange, reaction of **5b** with magnesium was slightly more successful in leading to the formation of three products, along with substantial decomposition (Scheme 5). The best results were obtained in THF, using three times sublimed magnesium rather than commercial magnesium turnings. The magnesium was first activated with 1,2-dibromoethane; after cooling of the reaction mixture to room temperature, **5b** was added and the reaction was followed by ^{31}P NMR spectroscopy. Two of the products were known: 3,4-dimethylphosphinine (**18**, $\delta(^{31}P)$ 191 ppm)[15] and 4,4′,5,5′-tetramethyl-2,2′-biphosphinine (**16**, $\delta(^{31}P)$ 181.3 ppm).[16] This compound was unambiguously identified by its proton-coupled ^{31}P NMR spectrum which showed an AA′BB′XX′ system. With the PH

(12) Alcaraz, J. M.; Mathey, F. *Tetrahedron Lett.* **1984**, *25*, 207.
(13) Reference 2, p 239.
(14) Nyulaszi, L; Szieberth, D; Veszpremi, T. *J. Org. Chem.* **1995**, *60*, 1647.
(15) Alcaraz, J. M.; Mathey, F. *Tetrahedron Lett.* **1984**, *25*, 4659.
(16) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1991**, *113*, 667.

Scheme 5

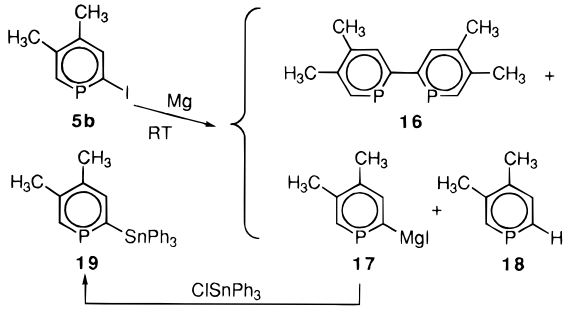


Table 1. Relative Intensities of ^{31}P NMR Signals during the Reaction of 5b with Magnesium in THF

time (h)	5b	18	16	17
2.5	6.50	1	0	1.83
5.75	0.34	1	0	1.57
21.0	0	1	0.16	0.59
25.0	0	1	0.20[a]	1.04[a]

[a] Due to the relatively large line width of **18**, these figures are not a good indication for relative amounts; actually, these amounts are smaller.

coupling constants given by Mathey for **16**,[16] simulation of the proton-coupled ^{31}P NMR spectrum exactly reproduced the experimentally obtained pattern. The third product was the desired phosphinine Grignard reagent **17** (δ(^{31}P) 229.0 ppm). This compound was identified by a reaction with triphenyltin chloride which gave the organotin derivative **19** (δ(^{31}P) 222.0 ppm), identical with a product obtained via an independent route.[4a]

Several observations may be of interest. First, it is remarkable that hardly any reaction occurred with diethyl ether instead of THF as solvent. Also, the degree of decomposition of **5b** increased when activation of magnesium with 1,2-dibromoethane was carried out in the presence of **5b**. Finally, when magnesium salts, formed by activation of magnesium with 1,2-dibromoethane, were removed by washing with THF, the reaction on subsequent addition of **5b** was very slow. This observation may indicate an initiating[17] or catalytic[18] role of magnesium bromide in the reaction of magnesium with **5b**. By calibration with triphenylphosphine as an internal standard, the absolute yields of **18**, **16**, and **17** were found to be 41.5, 1.3, and 19.2%, respectively; more than one-third (37%) of **5b** had decomposed.

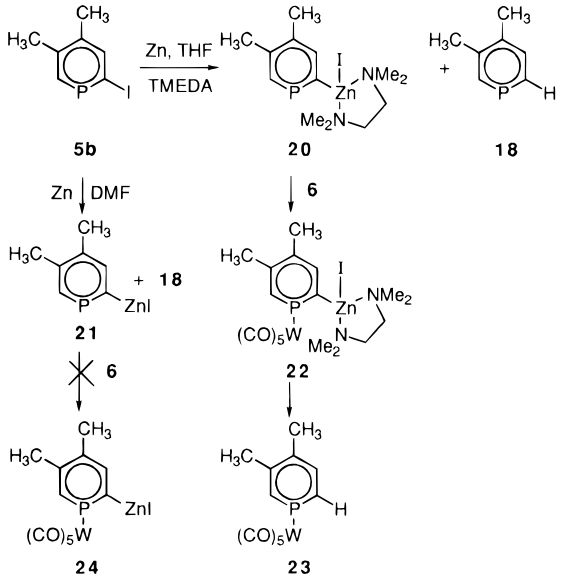
The reaction of **5b** with magnesium in the presence of triphenylphosphine turned out to be considerably slower (see Experimental Section) than in the absence of triphenylphosphine. A reaction mixture consisting of magnesium (4.11 mmol) in THF (5 mL) was activated with 1,2-dibromoethane (2.32 mmol). After addition of **5b** (1.16 mmol), the reaction was followed by ^{31}P NMR spectroscopy at room temperature during 25 h. The course of the reaction is presented in Table 1.

From Table 1 it follows that the conversion of **5b** is complete within 21 h. Furthermore, it is remarkable that the formation of **16** does not occur in the initial phase of the reaction but only after the amount of **5b** has diminished substantially and approaches zero.

(17) Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Non Metallic Substances*; Prentice-Hall: New York, 1954; p 56.

(18) Garst, J. F.; Lawrence, K. E.; Batlow, R.; Boone, J. R. *Inorg. Chim. Acta* **1994**, *222*, 365.

Scheme 6



Finally, the Grignard reagent **17** decomposed slowly at room temperature.

The course of the reactions discussed above are challenging from a mechanistic point of view. The formation of **18** and **17** can be explained by the radical mechanism of Grignard reagent formation.[17−19] The obvious possibility that **16** might be formed by a coupling reaction between **5b** and **17** is ruled out by the observation that **16** is not formed in the initial phase when **5b** and **17** are abundant. The alternative formation of **16** by nucleophilic attack of **17** on **18** is unlikely because nucleophilic attack on the phosphinine ring occurs at the phosphorus center.[13] More likely is the assumption that **17** decomposes (possibly under the influence of magnesium bromide and the excess of magnesium) under the formation of the 2-phosphininyl radical, which will yield **16** by radical coupling and **18** by hydrogen abstraction from the solvent.

Mathey *et al.* described that 2-chloro-4,5-dimethylphosphinine did not show any reaction with magnesium in refluxing THF under ultrasonic irradiation;[3b] the 2-bromo derivative proved to be equally inert. A reinvestigation showed that, in reaction of 2-bromo-4,5-dimethylphosphinine with magnesium alone, the phosphinine Grignard reagent could not be generated efficiently.[3d,e] On the other hand, trapping of the *in situ* generated Grignard species with silicon electrophiles under Barbier conditions lead to the formation of functionalized phosphinines in good yields.[3d,e] Therefore, the reaction of **5b** with magnesium is the first example of the direct reaction leading to an observable phosphinine Grignard reagent (**17**); this is possibly a consequence of the high reactivity of the carbon−iodine bond. However, interesting as the formation of **17** and that of **16** from **5b** may be from a mechanistic point of view, their yield is too low for preparative applications.

Organozinc Derivatives. The course of the metalation of **5b** with zinc in THF/TMEDA or DMF is depicted in Scheme 6. In THF, the selective formation of **20** (δ(^{31}P) 220.5 ppm) occurred at room temperature by reaction of **5b** with zinc dust (1.8 equiv) in the

(19) (a) Walborsky, H. M. *Acc. Chem. Res.* **1990**, *23*, 286. (b) Bickelhaupt, F. *J. Organomet. Chem.* **1994**, *475*, 1.

presence of TMEDA (1 equiv). The reaction required 20 h, after which the conversion of **5b** to **20** (and traces of **18**) was complete. The NMR spectroscopic characterization of **20** was performed on crystals obtained after cooling its THF solution for several days to −70 °C. Without TMEDA, zinc insertion of **5b** did not occur. Even prolonged heating of **5b** in THF at 60 °C with zinc dust resulted only in slow reduction of **5b** to **18**.

In DMF, the conversion of **5b** to **21** ($\delta(^{31}P)$ 222.6 ppm) and traces of **18** was achieved by reaction with zinc dust (2.8 equiv) during 20 h at room temperature. The organometallic phosphinine derivative turned out to be very stable; a sealed tube containing **21** in DMF-d_7 (prepared for NMR characterization) remained practically unchanged after several months at room temperature.

These results on zinc insertion reactions of **5b** are unique, as attempted insertion reactions with the 2-chloro and 2-bromo derivatives were unsuccessful.[3b] Comparison of the zinc insertions into iodobenzene and **5b** shows the latter to be more reactive; iodobenzene is converted to phenylzinc iodide for only 80% during 22 h at 55 °C in DMF.[5a] As the zinc insertion in THF/TMEDA has been described for an olefinic system only,[6] a direct comparison is not possible. Therefore, we carried out a zinc insertion with iodobenzene in THF/TMEDA at room temperature and quenched the reaction mixture with bromine; according to GCMS analysis, zinc insertion had not occurred. A possible explanation for these differences in reactivity between **5b** and iodobenzene might be the increased electron acceptor properties of the phosphinine ring compared with those of the benzene ring.[20] As the rate-determining step in the zinc insertion reaction is presumably a single electron transfer from zinc to the arene ring,[5a] **5b** would be expected to react faster than iodobenzene.

Whereas the zinc insertion into **5b** is successful in DMF and THF/TMEDA, the corresponding tungsten complex **7b** showed a disappointing behavior under the same reaction conditions. The desired zinc complexes **22** and **24** were not formed selectively; the ^{31}P NMR spectra showed many signals in the region 0−200 ppm. A different approach for the preparation of **22** and **24** is the reaction of **20** or **21** with (acetonitrile)pentacarbonyltungsten **6** (Scheme 6). This strategy failed in DMF; **24** was not obtained, but slow decomposition of **21** occurred. In THF/TMEDA, however, **22** ($\delta(^{31}P)$ 174.5 ppm, $^1J(PW) = 249.7$ Hz) was formed from **20** (containing a small amount of **18**) in moderate yield. The complexation procedure at room temperature required 20 to 30 h stirring when carried out with 1 equiv of **6** (yield 68−70%). With an excess (13%) of **6**, the complexation was complete within 15 h, and the yield was slightly higher (78%). Other phosphinines present in the final reaction mixture were **7b** (5.6%), **18** (4.3%), and **23** (3.5%). The formation of **22** was supported by ^1H and ^{13}C NMR spectra which were recorded in THF-d_8. Unfortunately, **22** decomposed slowly at room temperature. Following this process by NMR showed that, after 7 days, **22** was no longer present; **23** and two unidentified products ($\delta(^{31}P)$ 60.8 ppm, $^1J(PW) = 260.4$ Hz; 61.5 ppm, $^1J(PW) = 259.5$ Hz) were formed.

(20) Elschenbroich, C.; Nowotny, M.; Metz, B.; Massa, W.; Graulich, J. *Angew. Chem.* **1991**, *103*, 601.

Conclusions

The synthesis of 2-iodophosphinines and their pentacarbonyltungsten complexes is an interesting expansion of the chemistry of halophosphinines. The unique properties of the 2-iodophosphinines were illustrated by the synthesis of organozinc derivatives **20**−**22**, which cannot be obtained from the 2-bromo or 2-chloro analogues.

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 $LiAlH_4$, and CH_2Cl_2 was distilled from P_2O_5. Triethylamine was distilled from CaH_2, and PCl_3 was distilled before use. A solution of 1.6 M *n*-BuLi in hexane was commercially available and used as received. Sublimed magnesium was kindly provided by G. Schat. 2-Chloropropane and 2,3-dimethyl-1,3-butadiene were distilled before use. TMEDA was distilled from Na. DMF was distilled and stored on 4 Å molecular sieves. Zinc powder was activated with dilute HCl and thoroughly washed with oxygen-free water, ethanol, THF, and pentane.

NMR spectra were recorded at a Bruker AC 200 spectrometer at 200 MHz (^1H) or 50.32 MHz (^{13}C). For ^{31}P NMR spectroscopy a Bruker WM 250 was used operating at 100.26 MHz. Incidentally, ^1H, ^{13}C, or ^{31}P NMR experiments were carried out with a Bruker MSL 400, operating at 400 MHz (^1H), 100.64 MHz (^{13}C), or 161.9 MHz (^{31}P). The coupling constants (J) are given in Hz.

The direct inlet mass spectra were measured with a Finnigan MAT 90 (Bremen FRG), source temperature 150 °C (70 eV IP). The GCMS 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 analysis were carried out by Micro Analytisches Labor Pascher in Remagen, Germany. Melting points (uncorrected) were determined with melting point equipment of Pleuger after Dr. Tottoli.

Dichloro(diiodomethyl)phosphine (2). A solution of isopropylmagnesium chloride, prepared from Mg (twice sublimed, 5.37 g, 221 mmol), isopropyl chloride (35 mL, 274 mmol), and THF (60 mL), was added dropwise with a syringe to a solution of iodoform (80.46 g, 204 mmol) in THF (400 mL) at −95 °C. The resulting dark red solution was frozen with liquid nitrogen to −196 °C. Then a Schlenk tube containing freshly distilled PCl_3 (230 mL, 2.636 mol) was frozen with liquid nitrogen, too, and attached upside down upon the solid reaction mixture. By spontaneous warming, the PCl_3 was allowed to flow down slowly on top of the carbenoid mixture which was kept at −196 °C. After complete addition, the reaction mixture was allowed to warm to −100 °C and mechanical stirring was commenced as soon as possible. The reaction mixture became yellow and a large amount of colorless precipitate was formed within 15 min. The reaction mixture was warmed to −40 °C during 4 h and then quickly to room temperature, while the color changed gradually from yellow to brown orange. The volatile compounds were removed under reduced pressure, and the residue was extracted three times with pentane (640 mL) and filtered. After concentration of the pentane extracts to 300 mL, another filtration was carried out. Further removal of pentane from the filtrate under vacuum furnished crude **2** as a red brown oil. Attempted purification via distillation or crystallization did not improve the purity significantly. Therefore, the subsequent Diels−Alder reactions with a 1,3-butadiene were carried out with freshly prepared crude **2**, which, on the basis of ^{31}P NMR spectroscopy was approximately 70% pure. The main impurity, $\delta(^{31}P)$ 175 ppm, is presumably a

compound R-PCl_2, but it was not identified. Data for **2** are as follows. NMR (C_6D_6): $\delta(^1H)$ 4.34 (d, $^2J(PH) = 17.1$); $\delta(^{13}C\{^1H\})$ −19.1 (dd, $^1J(PC) = 84.9$, $\{^1J(CH) = 167.5\}$); $\delta(^{31}P\{^1H\})$ 155.2. HRMS (*m/e*): calcd for $CH^{35}Cl_2I_2P$, 367.7280; found, 367.7256. MS (EI): *m/e* 368 ($[M]^+$, 54), 333 ($[M - Cl]^+$, 15), 241 ($[M - I]^+$, 98), 206 ($[M - 2Cl - I]^+$, 15).

2-Iodophosphinine (5a). Compound **2** was prepared as described above from iodoform (177.2 g, 450 mmol). In this case, commercial isopropylmagnesium chloride was used. Crude **2** was obtained in a yield of 63% (104 g, 0.28 mol). Then 1,3-butadiene (350 g, 6.5 mol) was condensed into the reaction vessel. After dropwise addition of approximately 1 equiv of NEt_3 (39 mL, 0.28 mol) at −5 °C, a large amount of brown-red precipitate was formed in the yellow solution. As this made stirring difficult, THF (270 mL) was added. Then the rest of the NEt_3 (400 mL, 2.88 mol) was added dropwise within 3 h. Meanwhile, the temperature was allowed to rise to room temperature. After 16 h, the heterogeneous yellow brown mixture was evaporated and the residue extracted six times with pentane (800 mL). The combined extracts were concentrated to 100 mL and filtered. Distillation, first under normal pressure and finally under vacuum, furnished **5a** (slightly contaminated with 1,1-diiodoisobutane) as a yellow liquid (bp 45 °C/4 × 10^{-3} mbar) in a yield of 10% (10.8 g, 0.044 mol). Data for **5a** are as follows. NMR (C_6D_6): $\delta(^1H)$ 6.61 (ddt, $^4J(PH) = 4.3$, $^4J(HH_6) = 1.0$, $^3J(HH_5) = 8.4$, $^3J(HH_3) = 8.6$, 1H, H_4), 7.27 (apparent q, $^3J(PH) = 8.6$, $^3J(HH_4) = 8.4$, $^3J(HH_6) = 10.1$, 1H, H_5), 7.94 (ddd, $^2J(PH) = 38.8$, $^3J(HH_5) = 10.1$, $^4J(HH_4) = 1.0$, 1H, H_6), 7.95 (dd, $^3J(PH) = 5.3$, $^3J(HH_4) = 8.6$, 1H, H_3); $\delta(^{13}C\{^1H\})$ 124.9 (dt, $^1J(PC) = 77.5$, $\{^3J(CH_6) = 12.1\}$, $\{^3J(CH_4) = 12.1\}$, C_2), 130.7 (dddd, $^3J(PC) = 18.6$, $\{^1J(CH) = 159.6\}$, $\{^3J(CH_6) = 8.8$, $^2J(CH_3$ or $CH_5) = 2.0\}$, C_4), 131.8 (ddd, $^2J(PC) = 13.3$, $\{^1J(CH) = 158.3\}$, $\{^3J(CH) = 7.4\}$, C_5), 143.4 (dddt, $^2J(PC) = 14.5$, $\{^1J(CH) = 164.1\}$, $\{^3J(CH_5) = 7.8\}$, $\{^2J(CH_4) = 1.4\}$, $\{^4J(CH_6) = 1.4\}$, C_3), 159.4 (ddd, $^1J(PC) = 60.5$, $\{^1J(CH) = 165.6\}$, $\{^3J(CH_4) = 9.0\}$, C_6); $\delta(^{31}P\{^1H\})$ 233.1. MS (EI): *m/e* 222 ($[M]^+$, 20), 95 ($[M - I]^+$, 18). HRMS (*m/e*): calcd for C_5H_4IP, 221.9094; found, 221.907. Anal. Calcd for C_5H_4IP: C, 27.06; H, 1.82. Found: C, 26.94; H, 2.14.

2-Iodo-4,5-dimethylphosphinine (5b). To the crude mixture of **2**, freshly distilled 2,3-dimethyl-1,3-butadiene (300 mL, 2.65 mol) was added. After cooling of the mixture to 0 °C, NEt_3 (300 mL, 2.16 mol) was added dropwise during 5 h. A brown precipitate was formed, and the reaction mixture became red. The temperature was then raised gradually to room temperature. During 55 h the reaction was followed by ^{31}P NMR spectroscopy, which indicated the conversion of **4b** ($\delta(^{31}P)$ 94 ppm) to **5b** (impurity at ($\delta(^{31}P)$ 95 ppm, 7%). After the mixture was stirred, the volatile fraction was removed under vacuum. The residue was extracted four times with pentane (600 mL) and filtered. After concentration of the combined pentane fractions to 150 mL and filtration, the filtrate was subjected to distillation, first at atmospheric pressure to remove pentane and then under vacuum to obtain **5b**. A second distillation furnished pure **5b** as yellow crystals (mp 30 °C; bp 76 °C/10^{-3} mbar) in a yield of 32% (16.4 g, 65.7 mmol) relative to iodoform. Data for **5b** are as follows. NMR (C_6D_6): $\delta(^1H)$ 1.69 (d, $^5J(PH) = 3.7$, 3H, 4-CH_3), 1.74 (s, 3H, 5-CH_3), 7.69 (d, $^2J(PH) = 38.6$, 1H, H6), 7.96 (d, $^3J(PH) = 5.6$, 1H, H_3); $\delta(^{13}C\{^1H\})$ 21.5 (dq, $^4J(PC) = 1.9$, $\{^1J(CH) = 127.2\}$, $^1J(CC_4) = 43.7$, 4-CH_3), 22.7 (ddq, $^3J(PC) = 3.4$, $\{^3J(CH) = 6.3\}$, $\{^1J(CH) = 127.0\}$, $^1J(CC_5) = 42.6$, 5-CH_3), 121.0 (dd, $^1J(PC) = 71.4$, $\{^3J(CH) = 12.7\}$, $^1J(CC_3) = 55.6$, C_2), 141.4 (d, $^3J(PC) = 17.5$, $^1J(CC_3) = 58.7$, $^1J(C_4\text{-}CH_3) = 43.7$, C_4), 141.9 (d, $^2J(PC) = 14.8$, $^1J(C_5\text{-}CH_3) = 42.6$, $^1J(CC_6) = 55.3$, C_5), 145.7 (ddq, $^2J(PC) = 15.2$, $\{^1J(CH) = 165.8\}$, $\{^3J(CH) = 5.4\}$, $^1J(CC4) = 58.7$, $^1J(CC_2) = 55.6$, C_3), 159.7 (ddq, $^1J(PC) = 56.9$, $\{^1J(CH) = 152.8\}$, $\{^3J(CH) = 5.0\}$,$^1J(CC_5) = 55.3$, C_6); $\delta(^{31}P\{^1H\})$ 216.2. HRMS (*m/e*): calcd for C_7H_8IP, 249.9407; found, 249.9446. MS (EI): *m/e* 250 ($[M]^+$, 62), 123 ($[M - I]^+$, 11). Anal. Calcd for C_7H_8IP: C, 33.63; H, 3.23; I, 50.76; P, 12.39. Found: C, 33.58; H, 3.20; I, 50.4; P, 12.6.

(η^1-2-Iodophosphinine)pentacarbonyltungsten (7a). A solution of (acetonitrile)pentacarbonyltungsten (**6**) (7.2 g, 19.7 mmol) and **5a** (4.02 g, 16.3 mmol) in THF (150 mL) was stirred at room temperature for 49 h. After 31 h, 0.44 g of **6** (1.2 mmol) was added to drive the complexation of **5a** toward completion. Afterward, the dark green solution was evaporated and the residue was extracted with pentane (600 mL). Crystallization by cooling the extract to −70 °C furnished pure **7a** as brown yellow crystals (dec 81 °C) in a yield of 48% (4.31 g, 7.9 mmol). Data for **7a** are as follows. NMR (C_6D_6): $\delta(^1H)$ 6.20 (tdd, $^4J(PH) = 8.0$, $^3J(HH_5) = 8.1$, $^3J(HH_3) = 8.8$, $^4J(HH_6) = 1.3$, 1H, H_4), 6.89 (dddd, $^3J(PH) = 22.7$, $^3J(HH_6) = 10.1$, $^3J(HH_4) = 8.1$, $^4J(HH_3) = 1.0$, 1H, H_5), 7.48 (ddd, $^2J(PH) = 26.4$, $^3J(HH_5) = 10.1$, $^4J(HH_4) = 1.3$, 1H, H_6), 7.68 (ddd, $^3J(PH) = 16.3$, $^3J(HH_4) = 8.8$, $^4J(HH_5) = 1.0$, 1H, H_3); $\delta(^{13}C\{^1H\})$ 120.8 (dddt, $^1J(PC) = 2.0$, $\{^3J(CH_4) = 10.5\}$, $\{^3J(CH_6) = 13.4\}$, $\{^2J(CH_2) = 2.9\}$, $\{^4J(CH_5) = 2.9\}$, C_2), 127.6 (dddd, $^3J(PC) = 29.0$, $\{^1J(CH) = 163.2\}$, $\{^3J(CH_6) = 8.8\}$, $\{^2J(CH_3$ or $CH_5) = 1.5\}$, C_4), 135.7 (ddddd, $^2J(PC) = 16.5$, $\{^1J(CH) = 161.1\}$, $\{^3J(CH_3) = 8.2\}$, $\{^2J(CH_6$ or $CH_4) = 1.2\}$, $\{^2J(CH_4$ or $CH_6) = 2.3\}$, C_5), 146.2 (dddt, $^2J(PC) = 13.3$, $\{^1J(CH) = 165.2\}$, $\{^3J(CH_5) = 8.5\}$, $\{^4J(CH_6) = 1.4\}$, $\{^2J(CH_4) = 1.4\}$, C_3), 153.0 (ddddd, $^1J(PC) = 12.4$, $\{^1J(CH) = 162.5\}$, $\{^3J(CH_4) = 9.1\}$, $\{^2J(CH_5) = 2.1\}$, $\{^4J(CH_3) = 1.5\}$, C_6), 194.4 (d, $^2J(PC) = 9.3$, $^1J(WC) = 125.0$, CO [cis]), 198.5 (d, $^2J(PC) = 33.0$, CO [trans]); $\delta(^{31}P\{^1H\})$ 201.5 ($^1J(PW) = 285.6$). HRMS calcd for $C_{10}H_4O_5IP^{182}W$, 543.8323; found, 543.832. MS (EI): *m/e* 546 ($[M]^+$, 55), 518 ($[M - CO]^+$, 3), 490 ($[M - 2CO]^+$, 42), 462 ($[M - 3CO]^+$, 31), 434 ($[M - 4CO]^+$, 34), 406 ($[M - 5CO]^+$, 100). Anal. Calcd for $C_{10}H_4IO_5PW$: C, 22.0; H, 0.74; P, 5.67; I, 23.25; W, 33.68. Found: C, 21.85; H, 0.76; P, 5.46; I, 22.0; W, 33.8.

(η^1-2-Iodo-4,5-dimethylphosphinine)pentacarbonyltungsten (7b). During 18 h, a THF solution (200 mL) of **7b** (3.7 g, 14.8 mmol) and **6** (6.4 g, 17.5 mmol) was heated to 45−50 °C. After removal of THF under reduced pressure, the residue was extracted with pentane (200 mL) and crystallized by cooling the extract to −70 °C. Pure **7b** was obtained as brown yellow crystals (dec 126−7 °C) in a yield of 86% (7.36 g, 12.8 mmol). Data for **7b** are as follows. NMR (C_6D_6): $\delta(^1H)$ 1.50 (s, 3H, 5-CH_3), 1.54 (d, $^5J(PH) = 6.4$, 3H, 4-CH_3), 7.54 (d, $^2J(PH) = 25.6$, 1H, H_6), 7.73 (d, $^3J(PH) = 17.4$, 1H, H_3); $\delta(^{13}C\{^1H\})$ 21.1 (ddq, $^4J(PC) = 4.0$, $\{^3J(CH) = 4.0\}$, $\{^1J(CH) = 127.5\}$, 4-CH_3), 22.4 (ddq, $^3J(PC) = 9.5$, $\{^3J(CH) = 6.4\}$, $\{^1J(CH) = 128.0\}$, 5-CH_3), 117.0 (t, $^1J(PC) = 6.6$, $\{^3J(CH) = 6.6\}$, C_2), 138.7 (d, $^3J(PC) = 26.2$, C_4), 146.7 (d, $^2J(PC) = 16.7$, C_5), 148.1 (ddq, $^2J(PC) = 13.3$, $\{^1J(CH) = 161.9\}$, $\{^3J(CH) = 5.5\}$, C_3), 152.5 (ddq, $^1J(PC) = 14.7$, $\{^1J(CH) = 158.4\}$, $\{^3J(CH) = 5.2\}$, C_6), 194.7 (d, $^2J(PC) = 9.3$, $^1J(WC) = 125.1$, CO [cis]), 198.7 (d, $^2J(PC) = 32.3$, $^1J(WC) = 148.2$, CO [trans]); $\delta(^{31}P\{^1H\})$ 184.6 ($^1J(PW) = 280.4$). HRMS (*m/e*): calcd for $C_{12}H_8IO_5PW$, 571.8636; found, 571.861. MS (EI): *m/e* 574 ($[M]^+$, 32), 518 ($[M - 2CO]^+$, 18), 490 ($[M - 3CO]^+$, 62), 462 ($[M - 4CO]^+$, 20), 434 ($[M - 5CO]^+$, 62). Anal. Calcd for $C_{12}H_8IO_5PW$: C, 25.11; H, 1.41; I, 22.11; P, 5.40; W, 32.03. Found: C, 25.36; H, 1.47; I, 21.8; P, 5.46; W, 31.5.

(η^1-2-Iodo-4,5-dimethylphosphinine)pentacarbonylchromium (8). A mixture of di-*n*-butyl ether (50 mL), **5b** (0.38 g, 1.5 mmol), and $Cr(CO)_6$ (0.49 g, 2.2 mol) was heated at 140 °C for 5.5 h. A black precipitate was formed in the dark green solution. Removal of solvent under reduced pressure was followed by extraction of the residue with pentane (100 mL). Crystallization by cooling the extract to −70 °C furnished pure **8** as yellow crystals (dec 101 °C) in a yield of 12% (0.08 g, 0.18 mmol). Data for **8** are as follows. NMR (C_6D_6): $\delta(^1H)$ 1.50 (s, 3H, 5-CH_3), 1.55 (d, $^5J(PH) = 6.2$, 3H, 4-CH_3), 7.58 (d, $^2J(PH) = 26.2$, 1H, H_6), 7.70 (d, $^3J(PH) = 16.7$, 1H, H_3); $\delta(^{13}C\{^1H\})$ 21.0 (ddq, $^4J(PC) = 3.9$, $\{^3J(CH) = 4.5\}$, $\{^1J(CH) = 127.4\}$, 4-CH_3), 22.5 (ddq, $^3J(PC) = 9.1$, $\{^3J(CH) = 6.3\}$, $\{^1J(CH) = 127.8\}$, 5-CH_3), 118.9 (d, $^1J(PC) = 2.5$, C_2), 138.6 (d, $^3J(PC) = 25.5$, C_4), 146.4 (d, $^2J(PC) = 17.0$, C_5), 148.8 (ddq, $^2J(PC) = 14.1$, $\{^1J(CH) = 161.8\}$, $\{^3J(CH) = 5.4\}$, C_3), 153.0 (ddq, $^1J(PC) = 8.8$, $\{^1J(CH) = 157.8\}$, $\{^3J(CH)$

= 5.1}, C_6), 214.9 (d, ^2J(PC) = 17.2, CO [cis]), 220.9 (d, ^2J(PC) = 3.8, CO [trans]); $\delta(^{31}P\{^1H\})$ 230.9. MS (EI): *m/e* 442 ($[M]^+$, 22), 414 ($[M - CO]^+$, 3), 386 ($[M - 2CO]^+$, 13), 358 ($[M - 3CO]^+$, 15), 330 ($[M - 4CO]^+$, 31), 302 ($[M - 5CO]^+$, 100), 250 ($[M - Cr(CO)_5]^+$, 11). Anal. Calcd for $C_{12}H_8CrIO_5P$: C, 32.60; H, 1.82; I, 28.71; P, 7.01. Found: C, 32.36; H, 1.84; I, 27.10; P, 7.43.

(η^1-2-Lithiophosphinine)pentacarbonyltungsten (11a). A solution of **7a** (0.15 g, 0.27 mmol) in THF (3.0 mL) was cooled to −100 °C. After addition of 1.6 M *n*-BuLi (0.25 mL, 0.40 mmol), the mixture was vigorously stirred while the temperature was maintained between −90 and −100 °C. The resulting black solution was subjected to low temperature ^{31}P NMR measurements. NMR (THF) for **11**: $\delta(^{31}P\{^1H\})$ 176.9 (^1J(PW) = 235.2).

(η^1-2-(Triphenylstannyl)phosphinine)pentacarbonyltungsten (13a). A solution of **7a** (1.12 g, 2.05 mmol) in THF (10 mL) was cooled to −100 °C. Then 1.6 M *n*-BuLi (1.3 mL, 2.08 mmol) was added during 30 s while the temperature was maintained at −100 °C. After 2 min, a solution of $ClSnPh_3$ (0.90 g, 2.34 mmol) in THF (2 mL) was added during 10 s. Then the dark red reaction mixture was allowed to warm to room temperature. Evaporation of the reaction mixture under reduced pressure was followed by extraction of the residue with pentane (50 mL). Crystallization by cooling the extract to −70 °C furnished pure **13a** as light brown crystals (dec 67 °C) in a yield of 4% (0.07 g, 0.09 mmol) relative to **7a**. Data for **13a** are as follows. NMR (C_6D_6): $\delta(^1H)$ 6.70 (q, ^4J(PH) = 7.8, $^3J(HH_5)$ = 7.8, $^3J(HH_3)$ = 7.8, 1H, H_4), 7.00−7.30 (m, 9H, *meta,para*-$SnPh_3$), 7.40−7.60 (m, 7H, *ortho*-$SnPh_3$ + H_5), 7.95 (dd, ^3J(PH) = 27.3, ^3J(HH) = 7.8, 1H, H_3), 8.40 (dd, ^2J(PH) = 24.1, $^3J(HH_5)$ = 10.2, 1H, H_6); $\delta(^{13}C)$ 126.5 (d, ^3J(PC) = 39.4, C_4), 129.2 (s, $^3J(^{119}SnC)$ = 54.6, $^3J(^{117}SnC)$ = 52.5, $SnPh_3$ *meta*-C), 129.9 (s, ^4J(SnC) = 11.9, $SnPh_3$ *para*-C), 135.2 (d, ^2J(PC) = 31.8, C_5), 137.5 (s, ^2J(SnC) = 39.8, $SnPh_3$ *ortho*-C), 137.7 (d, ^3J(PC) = 2.7, $^1J(^{119}SnC)$ = 553.1, $^1J(^{117}SnC)$ = 528.7, $SnPh_3$ *ipso*-C), 147.1 (d, ^2J(PC) = 20.7, ^2J(SnC) = 11.8, C_3), 154.5 (d, ^1J(PC) = 7.9, ^3J(SnC) = 34.0, C_6), 162.7 (d, ^1J(PC) = 30.2, C_2), 195.4 (d, ^2J(PC) = 9.1, ^1J(WC) = 124.9, CO [cis]), 197.8 (d, ^2J(PC) = 29.2, CO [trans]); $\delta(^{31}P\{^1H\})$ 195.4 ($^2J(P^{119}Sn)$ = 193.7, $^2J(P^{117}Sn)$ = 185.5, ^1J(PW) = 269.7). HRMS (*m/e*): calcd for $C_{28}H_{19}O_5P^{116}Sn^{184}W$, 765.9501; found, 765.949. MS (EI): *m/e* 768 ($[M]^+$, 14), 684 ($[M - 3CO]^+$, 32), 628 ($[M - 5CO]^+$, 42). Anal. Calcd for $C_{28}H_{19}O_5PSnW$: C, 43.73; H, 2.49. Found: C, 43.54; H, 2.61.

(η^1-2-Lithio-4,5-dimethylphosphinine)pentacarbonyltungsten (11b). A solution of **7b** (0.10 g, 0.17 mmol) in THF (2.5 mL) was cooled to −100 °C. After addition of 1.6 M *n*-BuLi (0.11 mL, 0.18 mmol), the mixture was vigorously stirred while the temperature was maintained between −90 and −100 °C. The resulting dark red solution was subjected to low-temperature ^{31}P NMR measurements. NMR (THF) for **11b**: $\delta(^{31}P\{^1H\})$ 163.4 (^1J(PW) = 239.8).

(η^1-2-(Triphenylstannyl)-4,5-dimethylphosphinine)pentacarbonyltungsten (13b). To a cooled solution (−95 °C) of **7b** (0.88 g, 1.53 mmol) in THF (10 mL) was added 1.6 M *n*-BuLi (0.95 mL, 1.52 mmol) during 10 min. After 20 min of stirring, $ClSnPh_3$ (0.62 g, 1.61 mmol) was added to the dark red solution. After being stirred for 10 min at −90 °C, the reaction mixture was allowed to warm to room temperature. The solvents were removed from the resulting dark red solution, and the residue was extracted with pentane (50 mL). Crystallization by cooling the extract to −70 °C furnished pure **13b** as yellow crystals (mp 144−5 °C) in a yield of 49% (0.60 g, 0.75 mmol) relative to **7b**. Data for **13b** are as follows. NMR (C_6D_6): $\delta(^1H)$ 1.67 (d, ^5J(PH) = 6.2, 3H, 4-CH_3), 1.77 (s, 3H, 5-CH_3), 7.20−7.35 (m, 9H, *meta,para*-$SnPh_3$), 7.60−7.75 (m, 6H, *ortho*-$SnPh_3$), 7.86 (d, ^3J(PH) = 29.5, ^3J(SnH) = 66.6, 1H, H_3), 8.36 (d, ^2J(PH) = 23.7, ^4J(SnH) = 23.8, 1H, H_6); $\delta(^{13}C\{^1H\})$ 21.6 (dq, ^4J(PC) = 4.0, $\{^1J$(CH) = 127.5}, 4-CH_3), 23.0 (dq, ^3J(PC) = 8.2, $\{^1J$(CH) = 127.5}, 5-CH_3), 129.2 (d, $^3J(^{119}SnC)$ = 54.4, $^3J(^{117}SnC)$ = 52.4, $\{^1J$(CH) = 157.3}, $SnPh_3$ *meta*-C), 129.8 (dt, ^4J(SnC) = 11.7, $\{^1J$(CH) = 159.6}, $\{^3J$(CH) = 7.0}, $SnPh_3$ *para*-C), 137.5 (d, ^2J(SnC) = 38.4, $\{^1J$(CH) = 157.0}, $SnPh_3$ *ortho*-C), 136.9 (d, ^3J(PC) = 35.4, C_4), 137.9 (d, ^3J(PC) = 2.7, $^1J(^{119}SnC)$ = 551.0, $^1J(^{117}SnC)$ = 526.5, $SnPh_3$ *ipso*-C), 148.5 (d, ^2J(PC) = 15.5, C_5) 149.2 (ddq, ^2J(PC) = 20.8, $\{^1J$(CH) = 157.1}, $\{^3J$(CH) = 5.4}, C_3), 154.1 (ddq, ^1J(PC) = 10.4, ^3J(SnC) = 37.6, $\{^1J$(CH) = 158.4}, $\{^3J$(CH) = 5.4}, C_6), 159.0 (d, ^1J(PC) = 25.5, $^1J(^{119}SnC)$ = 404.6, $^1J(^{117}SnC)$ = 385.5, C_2), 195.7 (d, ^2J(PC) = 9.2, ^1J(WC) = 124.5, CO [cis]), 198.0 (d, ^2J(PC) = 28.7, ^1J(WC) = 145.9, CO [trans]); $\delta(^{31}P\{^1H\})$ 180.5 ($^2J(P^{117}Sn)$ = 186.9, $^2J(P^{119}Sn)$ = 195.8, ^1J(PW) = 266.2); $\delta(^{119}Sn)$ −107.6. HRMS (*m/e*): calcd for $C_{30}H_{23}O_5P^{120}Sn^{182}W$, 795.9814; found, 795.984. MS (EI): *m/e* 798 ($[M]^+$, 28), 770 ($[M - CO]^+$, 6), 712 ($[M - 3CO]^+$, 42), 656 ($[M - 5CO]^+$, 64), 579 ($[M - 5CO - Ph]^+$, 5). Anal. Calcd for $C_{30}H_{23}O_5PSnW$: C, 45.22; H, 2.89. Found: C, 45.28; H, 3.29.

2-(Iodomagnesio)-4,5-dimethylphosphinine (17) and 4,4′,5,5′-Tetramethyl-2,2′-biphosphinine (16). (a) In the Absence of Triphenylphosphine. To a mixture consisting of Mg (three times sublimed, 0.10 g, 4.11 mmol) and THF (5 mL) was added 1,2-dibromoethane (0.2 mL, 2.32 mmol). After the exothermal activation of Mg, the mixture was cooled to room temperature and **5b** (0.29 g, 1.16 mmol) was added during stirring. The reaction mixture became black, and a dark brown precipitate was formed. After 25 h of stirring at room temperature, ^{31}P NMR spectroscopy indicated the presence of **17**, **16**, and **18** in a ratio of 19.2:3.6:18.4.

(b) In the Presence of Triphenylphosphine. Reliable indications concerning the yield of the products and the degree of decomposition of **5b** were obtained by carrying out a reaction with triphenylphosphine as internal standard, assuming that triphenylphosphine is inert under the reaction conditions. Therefore, the relative molar ratio of **5b** and triphenylphosphine was related to their relative intensity in a ^{31}P NMR spectrum, recorded before the reaction of **5b** with magnesium. An intensity ratio of 3.22:1 (**5b**:triphenylphosphine) corresponded to a molar ratio of 1:1. This ratio, deduced from **5b**, was applied to all phosphinine derivatives formed later. In this experiment, magnesium (6.17 mmol) was activated with 1,2-dibromoethane (4.48 mmol) in THF (10 mL) in the presence of triphenylphosphine (0.95 mmol). After cooling of the mixture to room temperature, **5b** (1.12 mmol) was added after which the reaction was followed by ^{31}P NMR spectroscopy. After 6 days of stirring at room temperature, the black reaction mixture, in which a dark brown precipitate was present, contained **18**, **16**, and **17** in an absolute yield of 41.5, 1.3, and 19.2%. More than one-third (37%) of **5b** had decomposed. Another 6 days later, only 0.11 mmol (10%) of phosphinines was left: predominantly **18** and hardly any **16** and **17**. Data for **17** are as follows. NMR (THF): $\delta(^{31}P\{^1H\})$ 229.0 ($\{^2J$(PH) = ^3J(PH) = 26.7}). Data for **16** are as follows. NMR (C_6D_6): $\delta(^{31}P\{^1H\})$ 181.3. HRMS (*m/e*): calcd for $C_{14}H_{16}P_2$, 246.0727; found, 246.0752. MS (EI): *m/e* 246 ($[M]^+$, 100), 231 ($[M - CH_3]^+$, 33).

(4,5-Dimethylphosphininyl-κC^2)(iodo)(TMEDA)zinc (20). A reaction mixture consisting of **5b** (1.88 g, 7.52 mmol), TMEDA (2.29 g, 19.7 mmol), and zinc powder (2.86 g, 43.7 mmol) in THF (12 mL) was stirred for 19 h at room temperature. Approximately 8 mL of this solution was cooled to −70 °C. After several days, a precipitate was formed consisting of dark gray crystals, contaminated with some light brown powder and a small amount of zinc dust. After removal of supernatant, the precipitate was dried and subjected to NMR analysis. Data for **20** are as follows. NMR (C_6D_6): $\delta(^1H)$ 1.88 (s, 4H, NCH_2), 2.15 (s, 12H, NCH_3), 2.20 (s, 3H, 5-CH_3), 2.24 (d, ^5J(PH) = 3.4, 3H, 4-CH_3), 8.67 (d, ^2J(PH) = 31.9, 1H, H_6), 8.81 (d, ^3J(PH) = 18.7, 1H, H_3), ratio TMEDA/**20** 1:1; $\delta(^{13}C)$ 22.4 (d, ^3J(PC) = 1.8, 5-CH_3), 23.6 (d, ^4J(PC) = 1.8, 4-CH_3), 49.0 (s, NCH_3), 56.8 (s, NCH_2), 136.3 (d, ^3J(PC) = 29.8, C_4), 141.5 (d, ^2J(PC) = 15.1, C_3), 147.9 (d, ^2J(PC) = 16.3, C_5), 155.0 (d, ^1J(PC) = 63.2, C_6), 183.4 (d, ^1J(PC) = 86.6, C_2); $\delta(^{31}P\{^1H\})$ 220.5.

2-(Iodozincio)-4,5-dimethylphosphinine (21). A mixture containing **5b** (0.18 g, 0.7 mmol), zinc powder (0.19 g, 2.8 mmol), and DMF-d_7 (1 mL) was stirred at room temperature for 15 h. Then the dark red solution was separated from the excess of zinc powder and placed in an NMR tube which was subsequently sealed. Data for **21** are as follows. NMR (DMF-d_7): δ(^{1}H) 2.32 (d, ^5J(PH) = 3.3, 3H, 4-CH_3), 2.35 (s, 3H, 5-CH_3), 8.14 (d, ^3J(PH) = 18.8, 1H, H_3), 8.42 (d, ^2J(PH) = 31.6, 1H, H_6); δ(^{13}C{^{1}H}) 20.7 (dddq, ^4J(PC) = 1.7,{^3J(CH) = 6.0}, {^4J(CH) = 0.9}, {^1J(CH) = 125.6}, 4-CH_3), 20.9 (dddq, ^3J(PC) = 1.4, {^3J(CH) = 6.8}, {^4J(CH) = 1.4}, {^1J(CH) = 126.0}, 5-CH_3), 133.8 (d, ^3J(PC) = 29.7, C4), 139.6 (d, ^2J(PC) = 14.7, C_5), 143.8 (ddq, ^2J(PC) = 16.5), {^1J(CH) = 152.9}, {^3J(CH) = 5.1}, C_3), 154.2 (ddq, ^1J(PC) = 64.0, {^1J(CH) = 149.0}, {^3J(CH) = 5.1}, C_6), 184.4 (d, ^1J(PC) = 86.6, C_2); δ(^{31}P{^{1}H}) 222.6.

[(4,5-Dimethylphosphininyl-1κP,2κC^2)pentacarbonyltungsten](iodo)(TMEDA)zinc (22). A solution of **20** (3.16 mmol) in THF (6.2 mL) was added to a solution of **6** (1.17 g, 3.21 mmol) in THF (2 mL). After 23 h of stirring at room temperature, a small amount of yellow precipitate was formed in the dark red solution. Of this solution a small amount (2 mL) was evaporated under reduced pressure. Subsequent NMR measurements indicated complete decomposition after 7 days at room temperature. Data for **22** are as follows. NMR (THF-d_8): δ(^{1}H) 2.22 (s, 3H, 5-CH_3), 2.52 (d, ^5J(PH) = 9.9, 3H, 4-CH_3), 2.49 (s, 12H, NCH_3), 2.68 (s, 4H, NCH_2), 8.16 (d, ^3J(PH) = 40.4, 1H, H_3), 8.26 (d, ^2J(PH) = 21.2, 1H, H_6); δ(^{13}C) 21.9 (d, ^4J(PC) = 4.2, 4-CH_3), 22.8 (d, ^3J(PC) = 6.9, 5-CH_3), 49.2 (s, NCH_3), 57.3 (s, NCH_2), 134.5 (d, ^3J(PC) = 42.1, C4), 145,4 (d, ^2J(PC) = 16.5, C_5), 149.0 (d, ^2J(PC) = 24.1, C_3), 154.3 (s, C_6), 180.2 (d, ^1J(PC) = 45.3, C_2), 197.6 (d, ^2J(PC) = 9.5, CO [cis]), 200.8 (d, ^2J(PC) = 24.1, CO [trans]); δ(^{31}P{^{1}H}) 174.6 (^1J(PW) = 249.7).

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