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Thermal Conversion of 1-Alkynyl-1,2-dihydrophosphetes into Phosphinines

Narcis Avarvari, Pascal Le Floch, Claude Charrier, and François Mathey*

Laboratoire "Hétéroéléments et Coordination" URA 1499 CNRS, DCPH, Ecole Polytechnique, 91128, Palaiseau Cedex, France

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ABSTRACT

1-Alkynyl-1,2-dihydrophosphetes, as prepared by reaction of the appropriate titanacyclobutenes with alkynyldichlorophosphines, rearrange to the corresponding phosphinines via an original 4π-cycloreversion-6π-electrocyclization mechanism. The reaction of dimethyltitanocene with 1,4-diphenylbutadiyne affords a new 3-vinyltitanacyclobut-3-ene that can serve to prepare a 3-vinylphosphinine **6** *by the same route.*

INTRODUCTION

In previous work, we have shown that transient phosphahexatrienes, either free [1] or as P complexes [2], readily electrocyclize to give dihydrophosphinines whose aromatization eventually leads to phosphinines. Besides, several experimental results [3–7] and theoretical calculations [8] have established that appropriately substituted 1,2-dihydrophosphetes, either as free species or as P complexes, are in thermal equilibrium with the corresponding 1-phosphadienes. On the basis of these data, we suspected that the 1-alkenyl or the more readily accessible 1-alkynyl-1,2-dihydrophosphetes could be easily transformed into the corresponding phosphinines upon simple heating. This is the subject of our report.

RESULTS AND DISCUSSION

The necessary 1-alkynyl-1,2-dihydrophosphetes were synthesized according to the procedure described by Doxsee *et al.* [9] and Tumas *et al.* [10], via the reaction of 1-alkynyldichlorophosphines with titanacyclobutenes. The organometallic reagents were prepared by condensation of dimethyltitanocene with the appropriate alkynes (Scheme 1) [11,12].

When R = Ph, the resulting 1,2-dihydrophosphetes were obtained in ca. 60% yield and fully characterized by ^{1}H, ^{13}C, ^{31}P NMR, and mass spectrometry. When R = Et, the dihydrophosphetes were unstable and highly sensitive to oxidation. The yields were lower (ca. 35%), and the products were only identified by ^{31}P NMR spectroscopy and used after partial purification.

As expected, upon mild heating for several days in benzene, the dihydrophosphetes **1a–c** were indeed transformed into the corresponding phosphinines **2a–c** (Scheme 2).

The reaction works well when R = Ph (ca. 60% yield) and full characterization of **2a** and **2b** was carried out. When R = Et, the yield was much lower, and the phosphinine **2c** was only characterized by ^{31}P NMR spectroscopy: δ ^{31}P(**2c**) + 209.6 (toluene). The mechanism probably involves the electrocyclization of an intermediate phosphadiene (Scheme 3).

Dedicated to Professor Louis D. Quin as a tribute to an outstanding phosphorus chemist and a long-standing friend.

*To whom correspondence should be addressed.

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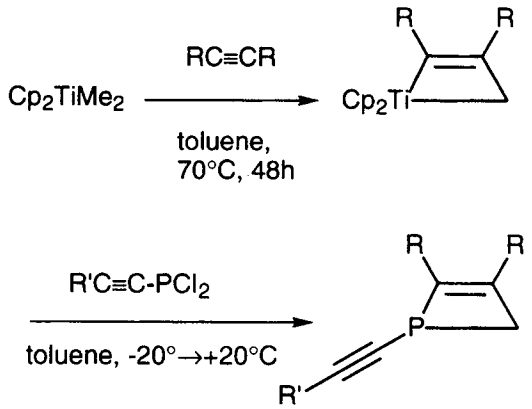
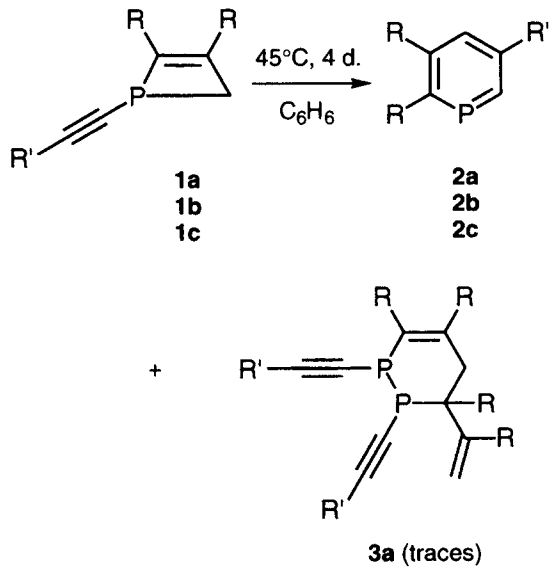


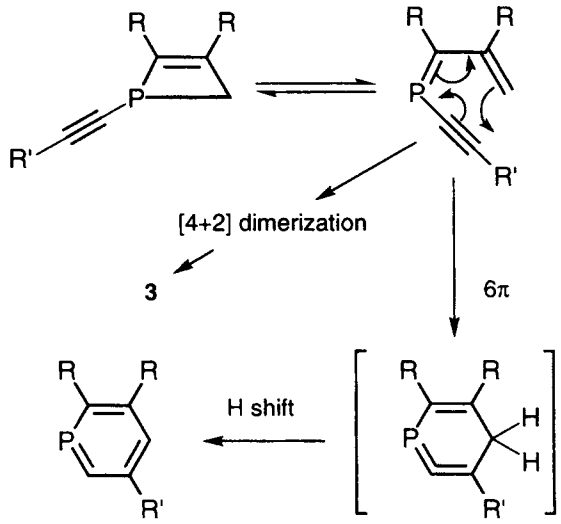
1a R = R' = Ph
1b R = Ph, R' = n-C_6H_{13}
1c R = Et, R' = Ph
1d R = Et, R' = n-C_6H_{13}

SCHEME 1



SCHEME 2

The transient formation of this phosphadiene was ascertained by the characterization of the [4+2] dimer **3a**. This compound was obtained as a minor by-product in the synthesis of **2a** and identified by mass spectrometry (molecular peak at *m/z* 648) and ^{31}P NMR in C_6D_6:δ ^{31}P (**3a**) − 27.3 and −49.3, ^1J (P–P) = 200 Hz (major diastereomer); −28.6 and −49.0, ^1J (P–P) = 198 Hz (minor diastereomer). Similar phosphadiene dimers have already been described in the literature [13].

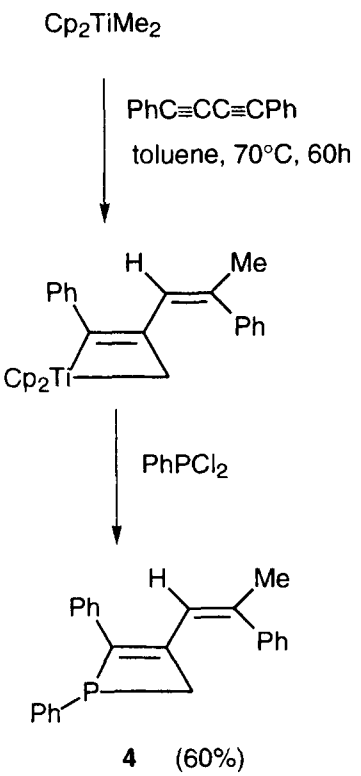


SCHEME 3

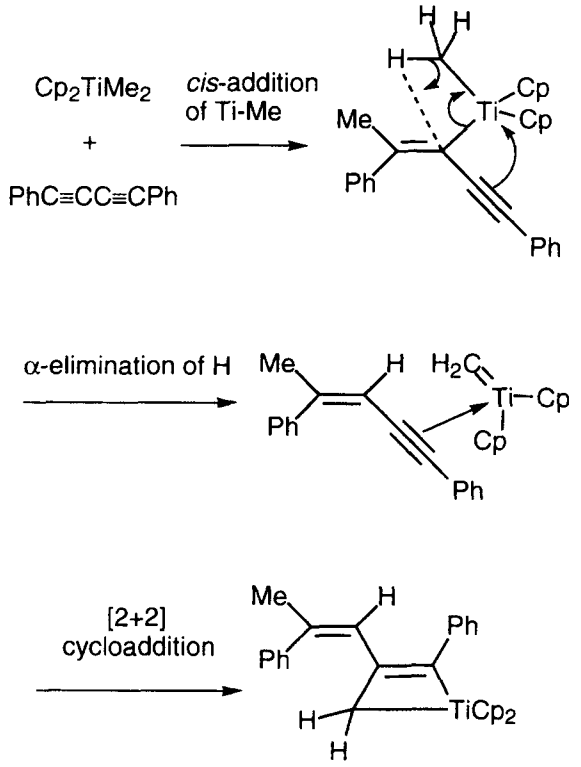
Having devised a new route to phosphinines, we then tried to apply it to the synthesis of 2,2'-biphosphinines whose applications in coordination chemistry are developing rapidly [14]. With this aim in mind, we investigated the reaction of dimethyltitanocene with 1,4-diphenyl-butadiyne. With a Cp_2TiMe_2/Ph_2C_4 ratio of 2:1, a complex and untractable mixture of products was obtained. With a 1:1 ratio, a well-defined titanacyclobutene was formed whose reaction with phenyldichlorophosphine gave the 1,2-dihydrophosphete **4** (Scheme 4).

The structure of **4** was established by ^1H, ^{13}C, ^{31}P NMR, and mass spectrometry. We also analyzed its P–$W(CO)_5$ complex. One of the key spectral features of **4** concerns the resonance of the vinylic hydrogen: δ(H) 6.5 (dq, ^4J (H–H) = 1.5 Hz, ^4J (H–P) = 1.4 Hz, =CH). Thus, both the methyl group and the vinylic hydrogen are situated on the same double bond. The *cis* disposition is not demonstrated, but the *cis* addition of Ti–CH_3 bonds to alkynes is a well-documented process [11]. The respective positions of the vinyl and the phenyl substituents on the ring carbons C_4 and C_3 results from the analysis of the spectral data of phosphinine **6** (see later). As demonstrated by Petasis and Fu [11], the dimethyltitanocene can either insert a C ≡ C triple bond into one of its Ti–CH_3 bonds or eliminate CH_4 to produce the Ti = CH_2 carbene complex that then gives a [2 + 2] cycloadduct with the C ≡ C triple bond. The formation of a 3-vinyltitanacyclobut-2-ene from one molecule of Cp_2TiMe_2 and one molecule of butadiyne combines the two processes. The most likely mechanism is proposed in Scheme 5.

The same chemistry when performed with



SCHEME 4



SCHEME 5

PhC ≡ C–PCl_2 afforded the 1,2-dihydrophosphete **5**. Upon prolonged heating at 65°C, **5** gave the expected phosphinine **6** (Scheme 6).

Both compounds **5** and **6** were fully characterized by ^1H, ^{13}C, ^{31}P NMR, and mass spectrometry. One of the key features of the ^{13}C spectrum of **6** is the presence of a phenyl C-ipso resonance at δ 143.3 that displays a strong coupling with phosphorus: ^2J (C–P) = 24.7 Hz. This strong coupling demonstrates that this phenyl group is located on one of the α positions of the ring. Otherwise, all the spectral parameters of **6** are quite normal.

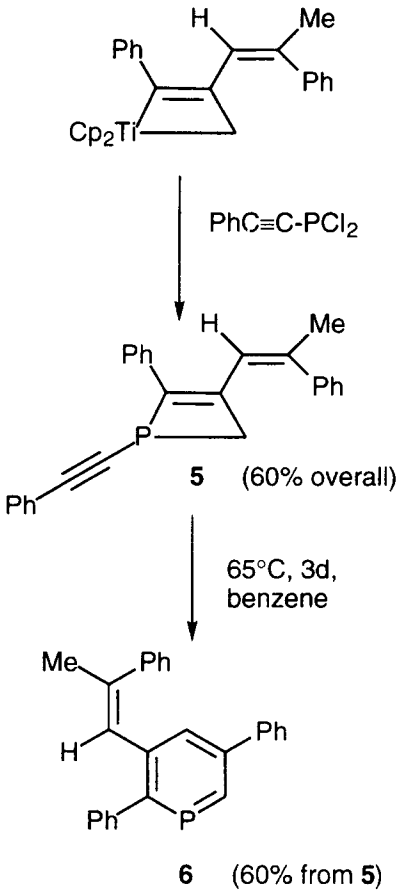
Even if this last series of experiments did not afford the expected 2,2′-biphosphinines, they demonstrate the versatility of this new synthesis of phosphinines while expanding the range of available titanacyclobutenes. It is probably possible to broaden the scope of this original 6π-electrocyclization to include the preparation of other heteroarenes.

EXPERIMENTAL SECTION

Reactions were carried out under nitrogen gas using oven-dried glassware. Dry THF, toluene, benzene, hexane, and diethyl ether were obtained by distillation from Na/benzophenone. Silica gel (70–230 mesh) was used for chromatographic separations. Nuclear magnetic resonance spectra were obtained on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^1H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants in Hertz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quadruplet; b, broad. Mass spectra were obtained at 70 eV with an HP 5989 B spectrometer coupled with HP 5890 chromatograph by the direct inlet method. Starting materials were obtained from commercial suppliers or prepared according to literature methods.

Synthesis of n-oct-1-ynyldichlorophosphine

To a three-necked flask (2 L) filled with nitrogen gas were added PCl_3 (0.364 mol) by syringe and dry diethyl ether (500 mL). After the flask had been in an ice cooled-water bath, diisopropylamine (2.711 mol) in dry diethyl ether (200 mL) was added dropwise from a dropping funnel, under mechanical stirring, and the resulting mixture was heated at reflux (40°C) for 7 days. Quantities of dry diethyl ether were added periodically. The reaction was monitored by ^{31}P NMR spectroscopy. Filtration under nitrogen



SCHEME 6

through a sintered glass filtration funnel covered with celite, followed by evaporation of solvent in vacuo, afforded bis-(diisopropylamino)chlorophosphine as a white crystalline solid.

A Schlenk flask containing 1-octyne (0.056 mol) in dry diethyl ether (40 mL) was cooled at −20°C, and BuLi (35.16 mL sol. 1.6 M in hexane) was added dropwise from a dropping funnel. The mixture was stirred for 1 hour at room temperature to allow the formation of *n*-octynyllithium, and bis-(diisopropylamino)chlorophosphino (0.056 mol) was then added. The formation of bis-(diisopropylamino)-*n*-octynylphosphine was complete after 4 days as resulted from its ^{31}P NMR spectrum. After this period, the flask was cooled at 0°C, and hydrogen chloride was bubbled into the reaction mixture for 5 minutes. The mother liquor was then removed from the white precipitate of diisopropylammonium chloride by filtration under nitrogen through a sintered glass filtration funnel covered with celite. Evaporation of solvent in vacuo, addition of dry hexane, filtration to exclude traces of salt, and, finally, removal of hexane in vacuo afforded *n*-octynyldichlorophosphine as a slightly oxygen-sensitive yellow oil. Phenylethynyldichlorophosphine was synthesized using an identical procedure, in 50% yield overall (see Ref. [15] for characterization).

n-Octynyldichlorophosphine, yield 45% ^{31}P NMR (C_6D_6) δ: 122.3. ^1H NMR (C_6D_6) δ: 1.01–1.08 (m, CH_3); 1.11–1.64 (m, 4 CH_2); 1.99–2.06 (m, $-CH_2-C\equiv$). ^{13}C NMR (C_6D_6) δ: 14.9 (s, CH_3); 20.8 (s, CH_2); 23.4 (s, CH_2); 28.3 (d, $^3J_{CP}$ = 2.9 Hz, CH_2); 29.3 (s, CH_2); 32.0 (s, CH_2); 81.0 (d, $^1J_{CP}$ = 73.0 Hz, $\equiv C-P$); 119.8 (d, $^2J_{CP}$ = 6.0 Hz, $-C\equiv$). MS *m/z* 211 (M^+).

General Procedure for the Synthesis of 1-Alkynyl-1,2-dihydrophosphetes (1a–d)

To a Schlenk flask containing a solution of Cp_2TiMe_2 (0.019 mol) in dry toluene (50 mL) were added diphenylacetylene (0.020 mol) for the synthesis of **1a** and **1b** and 3-hexyne (0.020 mol) for the synthesis of **1c** and **1d**. The Schlenk flask was wrapped in aluminum foil to exclude light and heated at 70°C for 48 hours, under magnetic stirring. The solution underwent a color change from orange to deep red, characteristically for titanacyclobutenes compounds that were not isolated for the subsequent utilization. The Schlenk solution, cooled at −20°C, was treated with phenylethynyldichlorophosphine (0.016 mol) for the synthesis of **1a** and **1c** and with *n*-octynyldichlorophosphine (0.016 mol) for the synthesis of **1b** and **1d**. The mother liquor containing 1-alkynyl-1,2-dihydrophosphetes was removed by cannula from titanocene dichloride, which precipitated as a red microcrystalline solid. Purification through a column of silica gel, eluting with a deoxygenated hexane/toluene (90:10) mixture, followed by evaporation of solvents in vacuo, afforded the dihydrophosphetes **1a–d**.

1-Phenylethynyl-3,4-diphenyl-1,2-dihydrophosphete (**1a**), yield 60%. ^{31}P NMR (C_6D_6) δ: −49.1. ^1H NMR (C_6D_6) δ: 2.79 (dd, $^2J_{H_AH_B}$ = 14.3 Hz, $^2J_{H_AP}$ = 10.6 Hz, H_A); 3.12 (dd, $^2J_{H_AH_B}$ = 14.3 Hz, $^2J_{H_BP}$ = 5.7 Hz, H_B); 7.00–8.00 (m, C_6H_5). ^{13}C NMR (C_6D_6) δ: 25.8 (d, $^1J_{CP}$ = 9.6 Hz, C_2); 85.5 (d, $^1J_{CP}$ = 57.1 Hz, $C_{1'}$); 107.4 (d, $^2J_{CP}$ = 10.4 Hz, $C_{1''}$); 122.9 (s, $C_{1''}$); 126.0–132.0 (m, CH, C_6H_5); 135.6 (d, $^1J_{CP}$ = 9.9 Hz, C_4); 136.8 (d, $^2J_{CP}$ = 4.6 Hz, $C_{4'}$); 141.7 (s, $C_{3'}$); 142.8 (d, $^1J_{CP}$ = 8.2 Hz, C_3). MS: *m/z* = 324 (M^+).

1-*n*-Octynyl-3,4-diphenyl-1,2-dihydrophosphete (**1b**), yield 60%. ^{31}P NMR (C_6D_6) δ: −48.3. ^1H NMR (C_6D_6) δ: 0.91–0.96 (m, CH_3); 1.11–1.44 (m, 4 CH_2); 2.10–2.16 (m, $-CH_2-C\equiv$); 2.71 (dd, $^2J_{H_AH_B}$ = 14.2 Hz, $^2J_{H_AP}$ = 10.5 Hz, H_A); 3.02 (dd, $^2J_{H_AH_B}$ = 14.2 Hz, $^2J_{H_BP}$ = 5.5 Hz, H_B); 7.00–7.60 (m, C_6H_5). ^{13}C NMR (C_6D_6) δ: 14.9 (s, CH_3); 21.2 (s, CH_2); 23.5 (s, CH_2); 26.6 (d, $^1J_{CP}$ = 10.3 Hz, C_2); 27.8 (s, CH_2); 29.3 (d, $^3J_{CP}$ = 4.1 Hz, $C_{1''}$); 32.2 (s, CH_2); 79.3 (d, $^1J_{CP}$ = 51.4 Hz, $C_{1'}$); 110.6 (d, $^2J_{CP}$ = 10.1 Hz, $C_{1''}$); 127.2–

130.1 (m, CH, C_6H_5); 136.8 (d, $^1J_{CP}$ = 10.3 Hz, C_4); 137.9 (d, $^2J_{CP}$ = 4.7 Hz, $C_{4'}$); 143.0 (d, $^1J_{CP}$ = 8.5 Hz, C_3); 143.6 (s, $C_{3'}$). MS: *m/z* = 332 (M^+).

1-Phenylethynyl-3,4-diethyl-1,2-dihydrophosphete (**1c**), yield 35%. ^{31}P NMR (C_6D_6) δ: −42.5.

1-*n*-Octynyl-3,4-diethyl-1,2-dihydrophosphete (**1d**), yield 35%. ^{31}P NMR (C_6D_6) δ: −41.3

General Procedure for the Synthesis of Phosphinines (**2a–c**)

A Schlenk flask containing a solution of 1,2-dihydrophosphetes **1a–c** (0.005 mol) in dry benzene (15 mL) was heated at 45°C for 4 days, under stirring. The reaction was monitored periodically by ^{31}P NMR spectroscopy. At the end of the reaction, celite (2 g) was then added, and the solvent was evaporated, yielding a brown powder that was deposited onto the top of a short silica-gel-packed flash column for chromatography. In each case, phosphinines **2a–c** were eluted with a deoxygenated hexane/toluene (90:10) mixture and recovered as yellow solids after the evaporation of solvents. After purification of **2a**, the [4 + 2] dimer **3a** was also isolated, in traces, by elution with a deoxygenated hexane/toluene (60:40) mixture.

2,3,5-Triphenylphosphinine (**2a**), yield 60%. ^{31}P NMR (C_6D_6) δ: 210.1 ($^2J_{PH_6}$ = 38 Hz). ^{1}H NMR (C_6D_6) δ: 7.15–7.61 (m, C_6H_5); 7.92 (dd, $^4J_{H_4H_6}$ = 1.7 Hz, $^4J_{H_4P}$ = 2.9 Hz, H_4); 9.00 (dd, $^4J_{H_4H_6}$ = 1.7 Hz, $^2J_{H_6P}$ = 37.9 Hz, H_6). ^{13}C NMR (C_6D_6) δ: 126.3–131.5 (m, CH, C_6H_5); 134.0 (d, $^3J_{CP}$ = 14.2 Hz, C_4); 143.1 (d, $^3J_{CP}$ = 2.8 Hz, $C_{5'}$); 143.6 (s, $C_{3'}$); 143.7 (d, $^2J_{CP}$ = 24.5 Hz, $C_{2'}$); 146.9 (d, $^2J_{CP}$ = 14.1 Hz, C_5); 148.0 (d, $^2J_{CP}$ = 11.5 Hz, C_3); 153.0 (d, $^1J_{CP}$ = 53.5 Hz, C_6); 169.0 (d, $^1J_{CP}$ = 53.3 Hz, C_2). MS: *m/z* = 324 (M^+).

2,3-Diphenyl-5-*n*-hexylphosphinine (**2b**), yield 60%. ^{31}P NMR (C_6D_6) δ: 208.6 ($^2J_{PH_6}$ = 40.3 Hz). ^{1}H NMR (C_6D_6) δ: 1.00–1.06 (m, CH_3); 1.37–1.7 (m, 4 CH_2); 2.67 (t, CH_2-C_5); 7.0–7.5 (m, C_6H_5); 7.55–7.6 (m, H_4); 8.6 (dd, $^4J_{H_4H_6}$ = 1.5 Hz, $^2J_{H_6P}$ = 38.8 Hz, H_6). ^{31}C NMR (C_6D_6) δ: 14.5 (s, CH_3); 17.7 (s, CH_2); 23.2 (s, CH_2); 29.6 (s, CH_2); 32.2 (s, CH_2); 39.3 (d, $^3J_{CP}$ = 3.1 Hz, $C_{5'}$); 126.6–131.0 (m, CH, C_6H_5); 134.7 (d, $^3J_{CP}$ = 14.2 Hz, C_4); 142.7 (s, $C_{3'}$); 143.4 (d, $^2J_{CP}$ = 24.4 Hz, $C_{2'}$); 147.1 (d, $^2J_{CP}$ = 14.1 Hz, C_5); 148.1 (d, $^2J_{CP}$ = 11.5 Hz, C_3); 153.6 (d, $^1J_{CP}$ = 53.5 Hz, C_6); 166.8 (d, $^1J_{CP}$ = 53.3 Hz, C_2). MS: *m/z* = 332 (M^+).

2,3-Diethyl-5-phenylphosphinine (**2c**), yield 20%. ^{31}P NMR (toluene) δ: 209.6.

General Procedure for the Synthesis of 1,2-Dihydrophosphetes (**4,5**)

To a Schlenk flask containing Cp_2TiMe_2 (0.019 mol) in dry toluene (50 mL) was added 1,4-diphenylbutadiyne (0.020 mol). The flask was wrapped in aluminum foil and heated at 70°C for 60 hours. The resulting deep-red solution was then cooled at −20°C and treated with phenyldichlorophosphine (0.016 mol) for the synthesis of **4** and phenylethynyldichlorophosphine (0.016 mol) for the synthesis of **5** (in each case the dichlorophosphine being added with a syringe). After warming to room temperature, the mother liquor, which contained the dihydrophosphete, was separated from Cp_2TiCl_2 by cannula. After addition of celite (3 g), the solvent was evaporated, yielding a brown powder that was deposited onto the top of a short silica-gel-packed flash column for chromatography. Dihydrophosphetes **4** and **5** were then eluted with a deoxygenated hexane/toluene (90:10) mixture and recovered as yellow solids after evaporation of solvents.

1,4-Diphenyl-3-*Z*-(2′-methyl-2′-phenyl)vinyl-1,2-dihydrophosphete (**4**), yield 60%. ^{31}P NMR (C_6D_6) δ: −9.6 ^{1}H NMR (C_6D_6) δ: 2.05 (d, $^4J_{HH}$ = 1.5 Hz, CH_3); 2.39 (dd, $^2J_{H_AH_B}$ = 15.2 Hz, $^2J_{H_BP}$ = 4.1 Hz, H_B); 2.78 (dd, $^2J_{H_AH_B}$ = 15.2 Hz, $^2J_{H_AP}$ = 10.1 Hz, H_A); 6.50 (b s, H vinyl); 7.10–7.90 (m, C_6H_5). ^{13}C NMR (C_6D_6) δ: 23.3 (s, CH_3); 29.5 (d, $^1J_{CP}$ = 7.7 Hz, C_2); 127.0–129.6 (m, CH, C_6H_5, vinyl); 133.2 (d, $^2J_{CP}$ = 18.3 Hz, CH ortho-P); 136.7 (d, $^1J_{CP}$ = 10.9 Hz, C_4); 137.1 (d, $^2J_{CP}$ = 2.6 Hz, $C_{4'}$); 138.5 (s, $C_{3''}$); 139.8 (d, $^1J_{CP}$ = 33.5 Hz, $C_{1'}$); 144.8 (s, $C_{3''}$); 147.3 (d, $^2J_{CP}$ = 7.2 Hz, C_3). MS: *m/z* = 340 (M^+).

1-Phenylethynyl-3-*Z*-(2′-methyl-2′-phenyl)vinyl-4-phenyl-1,2-dihydrophosphete (**5**), yield 60%. ^{31}P NMR (C_6D_6) δ: −43.2. ^{1}H NMR (C_6D_6) δ: 1.97 (d, $^4J_{HH}$ = 1.5 Hz, CH_3); 2.67 (dd, $^2J_{H_AH_B}$ = 15.0 Hz, $^2J_{H_AP}$ = 11.0 Hz, H_A); 2.94 (dd, $^2J_{H_AH_B}$ = 15.0 Hz, $^2J_{H_BP}$ = 5.2 Hz, H_B); 6.44 (bs, H vinyl); 7.04–7.84 (m, C_6H_5). ^{13}C NMR (C_6D_6) δ: 23.0 (s, CH_3); 26.9 (d, $^1J_{CP}$ = 10.8 Hz, C_2); 88.7 (d, $^1J_{CP}$ = 53.7 Hz, $C_{1'}$); 108.7 (d, $^2J_{CP}$ = 10.6 Hz, $C_{1''}$); 124.1 (s, $C_{1''}$); 126.1–129.5 (m, CH, C_6H_5, vinyl); 135.9 (d, $^1J_{CP}$ = 10.6 Hz, C_4); 136.5 (d, $^2J_{CP}$ = 4.6 Hz, $C_{4'}$); 138.2 (s, $C_{3''}$); 142.3 (s, $C_{3''}$); 147.4 (d, $^2J_{CP}$ = 7.5 Hz, C_3). MS: *m/z* = 364 (M^+).

Synthesis of P–W(CO)$_5$ Complex of the Dihydrophosphete 4

A solution of W(THF)$(CO)_5$ (15 mL, 0.006 mol), prepared by irradiation of $W(CO)_6$ in THF, was added to a Schlenk flask containing 1,2-dihydrophosphete **4** (0.005 mol). After 1 hour of stirring at room temperature, celite (1 g) was added to the crude mixture, and the solvent was removed in vacuo yielding a yellow solid. Complex **4**-$W(CO)_5$ was purified by chromatography with a hexane/CH_2Cl_2 (1:1) mixture. After evaporation of solvents, **4**-$W(CO)_5$ was recovered as a yellow oil.

1,4-Diphenyl-1-pentacarbonyltungsten-3-*Z*-(2′-methyl-2′-phenyl)vinyl-1,2-dihydrophosphete, yield 90%. ^{31}P NMR ($CDCl_3$) δ: 14.0. ^1H NMR ($CDCl_3$) δ: 2.06 (d, $^4J_{HH}$ = 1.5 Hz, CH_3); 2.62 (dd, $^2J_{H_AH_B}$ = 15.8 Hz, $^2J_{H_BP}$ = 9.6 Hz, H_B); 2.98 (dd, $^2J_{H_AH_B}$ = 15.8 Hz, $^2J_{H_AP}$ = 2.2 Hz, H_A); 6.50 (dq, $^4J_{HH}$ = 1.5 Hz, $^4J_{HP}$ = 1.4 Hz, H vinyl); 7.05–7.70 (m, C_6H_5). ^{13}C NMR ($CDCl_3$) δ: 23 (s, CH_3); 36.3 (d, $^1J_{CP}$ = 38.0 Hz, C_2); 127.0–131.6 (m, CH, C_6H_5, vinyl); 133.3 (d, $^2J_{CP}$ = 7.3 Hz, $C_{4'}$); 135.3 (d, $^4J_{CP}$ = 4.0 Hz, $C_{3''}$); 135.4 (d, $^1J_{CP}$ = 35.0 Hz, C_4); 137.1 (s, $C_{3''}$); 142.3 (d, $^1J_{CP}$ = 41.1 Hz, $C_{1'}$); 148.8 (d, $^2J_{CP}$ = 8.0 Hz, C_3); 196.6 (d, $^2J_{CP}$ = 7.0 Hz, 4 CO eq.); 199.1 (d, $^2J_{CP}$ = 22.7 Hz, CO ax.). MS: m/z = 664 (M^+).

Synthesis of Phosphinine (6)

A solution of 1,2-dihydrophosphete **5** (0.006 mol) in dry benzene (15 mL) was stirred at 65°C for 3 days, in a Schlenk flask. The reaction was monitored by ^{31}P NMR spectroscopy. After evaporation of benzene, phosphinine **6** was purified by chromatography under nitrogen (see purification of phosphinines **2a** and **2b**) with a hexane/toluene (90:10) mixture and recovered as a yellow oil.

2,5-Diphenyl-3-(2′-methyl-2′-phenyl)vinylphosphinine (**6**), yield 60%. ^{31}P NMR (C_6D_6) δ: 210.0 ($^2J_{PH_6}$ = 38.9 Hz). ^1H NMR (C_6D_6) δ: 1.86 (d, $^4J_{HH}$ = 1.5 Hz, CH_3); 6.38 (q, $^4J_{HH}$ = 1.5 Hz, H vinyl); 6.94–7.68 (m, C_6H_5); 7.73 (dd, $^4J_{H_4H_6}$ = 1.7 Hz, $^4J_{H_4P}$ = 3.0 Hz, H_4); 8.87 (dd, $^4J_{H_4H_6}$ = 1.7 Hz, $^2J_{H_6P}$ = 37.9 Hz, H_6). ^{13}C NMR (C_6D_6) δ: 27.5 (s, CH_3); 126.3–131.1 (m, CH, C_6H_5, vinyl); 132.4 (d, $^3J_{CP}$ = 14.5 Hz, C_4); 138.2 (s, $C_{3''}$); 140.8 (s, $C_{3'}$); 142.9 (d, $^3J_{CP}$ = 2.7 Hz, $C_{5'}$); 143.3 (d, $^2J_{CP}$ = 24.7 Hz, $C_{2'}$); 147.2 (d, $^2J_{CP}$ = 14.1 Hz, C_5); 148.7 (d, $^2J_{CP}$ = 12.0 Hz, C_3); 153.4 (d, $^1J_{CP}$ = 54.4 Hz, C_6); 168.3 (d, $^1J_{CP}$ = 52.9 Hz, C_2). MS: m/z = 364 (M^+).

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