Investigations of the Synthesis of 1,2-Diphosphinines

Ngoc Hoa Tran Huy,* Hélène Vong, and François Mathey*

Laboratoire "Hétéroéléments et Coordination", UMR CNRS 7653, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

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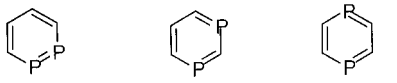
Several 1,2-disubstituted 3,6-bis(trimethylsilyl)-1,2-dihydro-1,2-diphosphinine complexes were prepared in a series of reactions starting from the palladium-catalyzed head-to-head dimerization of a 1-(2-ethoxycarbonylethyl)-2-trimethylsilylphosphirene $W(CO)_5$-complex. The $P-CH_2CH_2CO_2Et$ bonds were cleaved by ^tBuOK in THF to give the corresponding P-anions. The most significant products were the $PCl-P(CH_2CH_2CO_2Et)$ (**4**), $PH-P(OH)$ (**5**), and $PH-P(CH_2Ph)$ (**8**) complexes. The thermolysis of the $P(CH_2Ph)-P(CH_2Ph)$ complex (**9**) led to the corresponding phosphole complex **11** by extrusion of one phosphorus unit. Apparently, the postulated aromatic 1,2-diphosphinines are able to evolve toward other products via low-energy pathways.

Introduction

Two recent theoretical studies have pointed out that the presently unknown 1,2-diphosphinines (**A**) display an aromatic stabilization energy of the same order of magnitude as their known 1,3- (**B**) and 1,4-isomers (**C**).[1,2] In fact, both studies predict that the 1,2-isomer is ca. 5−10 kcal mol^{-1} lower in energy than the corresponding 1,3- and 1,4-species. Nonetheless, 1,2-diphosphinines remain conspicuous by their absence from the literature,[3] and the authors of the first theoretical study have suggested that inappropriate synthetic procedures could be responsible for that situation.[1] In this report, we wish to present our own attempts aimed at the synthesis of a 1,2-diphosphinine. Since complexation by pentacarbonyltungsten is known to increase the kinetic stability of P═P double bonds,[4] we decided to work in the coordination sphere of tungsten and to base our approach on the versatile chemistry of electrophilic terminal phosphinidene complexes $[RP-W(CO)_5]$.[5]



(**A**) (**B**) (**C**)

Results and Discussion

A head-to-head dimerization of phosphirenes leading to 1,2-dihydro-1,2-diphosphinines has been recently described by our group.[6] This observation gave us an ideal starting point for our synthetic work. A phosphirene with a good leaving group at phosphorus (**1**) was first synthesized as shown in Scheme 1. Phosphirene **1** was then dimerized in the presence of a palladium(0) catalyst using our previous protocol. The 1,2-dihydro-1,2-diphosphinine was mainly obtained as a bis-complex (**2**), the mono-complex appearing only as a minor byproduct (20% yield, ^{31}P NMR δ −34.2 (P−W) and −88.6, $^1J_{(P-P)} = 227$ Hz) contrary to our earlier experiments. We assume that the stereochemistry of the P_2 unit of **2** is *cis*, as in our previous work, but this point has not been confirmed. Treating **2** with 1 equiv of ^{t}BuOK in THF induces a clean dealkylation to the monoanion **3**.[7] The transformation was conveniently followed by ^{31}P NMR, where the resonance of **2** at ca. 3 ppm is quantitatively replaced by an AX system: δ_A −30.4, $^1J_{(P-P)} = 320$ Hz, $^1J_{(P-W)} = 227.4$ Hz ($P-CH_2$); δ_X −116.6, $^1J_{(P-W)} = 78.4$ Hz (P^-). The small direct coupling between P^- and tungsten confirms the presence of the negative charge.[8] The next step of our program involved the transformation of the P-anion **3** into the corresponding chlorophosphine. A preliminary attempt with S_2Cl_2 gave poor yields of the corresponding P−Cl compound **4**. A report by Kovar, Rausch, and Rosenberg[9] on the transformation of 1,1′-dilithio- into 1,1′-dibromoferrocene by reaction with tosyl bromide led us to investigate the reaction of **3** with tosyl chloride. A clean transformation into **4** was observed in 77% isolated yield. The most significant spectroscopic characteristics for **4** are the ^{31}P NMR data [δ ($P-CH_2$) 22.2, $^1J_{(P-W)} = 237$ Hz, $^1J_{(P-P)} = 173$ Hz; δ (P−Cl) 107.1, $^1J_{(P-W)} = 262$ Hz] and the mass spectrum [(^{35}Cl, ^{184}W)

(1) Colombet, L.; Volatron, F.; Maître, P.; Hiberty, P. C. *J. Am. Chem. Soc.* **1999**, *121*, 4215.
(2) Priyakumar, U. D.; Sastry, G. N. *J. Am. Chem. Soc.* **2000**, *122*, 11173.
(3) As far as we know, the unsuccessful synthesis of a diphosphaphenanthrene is the only described attempt to prepare a 1,2-diphosphaarene: van den Winkel, Y.; van der Laarse, J.; de Kanter, F. J. J.; van der Does, T.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Heteroat. Chem.* **1991**, *2*, 17.
(4) See, for example, the stabilization of dichlorodiphosphene Cl_2P_2: Vogel, U.; Stösser, G.; Scheer, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1443.
(5) Reviews: Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *27*, 275. Mathey, F. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, 1990; p 38. Dillon, K. B.; Mathey, F.; Nixon, J. F. In *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998; p 19.
(6) Tran Huy, N. H.; Ricard, L.; Mathey, F. *Chem. Commun.* **2000**, 1137.
(7) Base-catalyzed addition of secondary phosphines to activated C═C double bonds is a classical reaction. The reverse reaction can be observed whenever the resulting P-anion is somewhat stabilized, see for example ref 11.
(8) For example: $^1J_{(P-W)} = 68$ Hz for $[H_2LiP-W(CO)_5]$: Nief, F.; Mercier, F.; Mathey, F. *J. Organomet. Chem.* **1987**, *328*, 349.
(9) Kovar, R. F.; Rausch, M. D.; Rosenberg, H. *Organomet. Chem. Synth.* **1970/1971**, *1*, 173.

10.1021/om010682e CCC: $22.00
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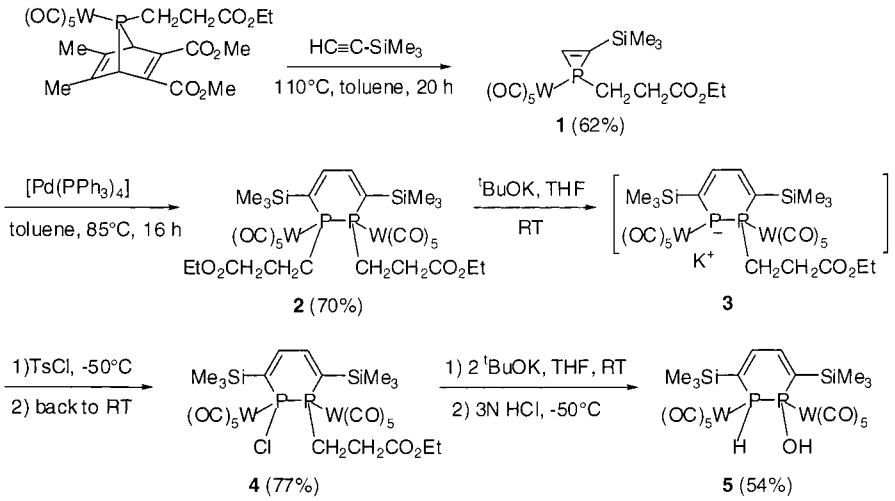
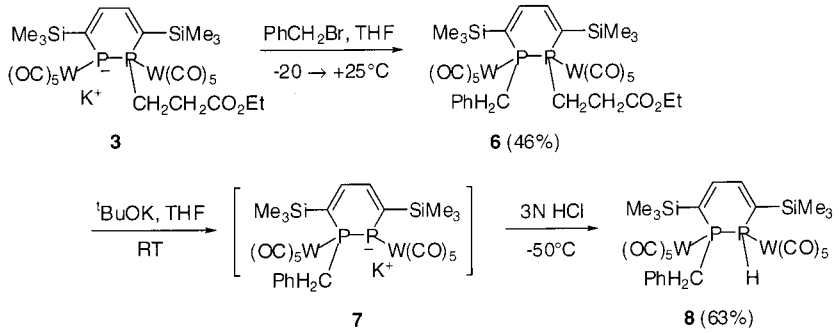
Scheme 1



Scheme 2



m/*z* 903 (M − 5CO, 6%), 819 (M − 8CO, 9%), 763 (M − 10CO, 9%), 578 (M − 10CO − W, 65%), 543 (M − 10CO − W − Cl, 100%)]. Complex **4** was then subjected to attack by ^{t}BuOK. The first experiments were done at −78 °C in THF with 1 equiv of base. We reasoned that the nucleophilic substitution at the P−Cl bond would be slow because of the steric hindrance at phosphorus and that proton abstraction from the CH_2CO_2Et group would be preferred. This is not the case. The initial product of the reaction shows the following ^{31}P NMR characteristics: AX system, δ_A + 54, δ_B −3, $^1J_{(P-P)}$ = 134 Hz. These data are not consistent with the formation of the expected P(Cl)−P$^-$ anion, but more in line with a nucleophilic attack at P−Cl. Thus, we were obliged to work with 2 equiv of ^{t}BuOK. At room temperature, the reaction cleanly leads to a major product having the following ^{31}P NMR characteristics: AX system, δ_A + 27, δ_X −129, $^1J_{AX}$ = 170 Hz. An anionic species is thus formed. Protonation at low temperature then yields the PH−P(OH) derivative **5**, which was isolated in 54% yield. The ^{31}P data of **5** are as follows: δ (P−H) −32.8, $^1J_{(P-P)}$ = 124.9 Hz, $^1J_{(P-H)}$ = 344.7 Hz; δ (P(OH)) 84.7 (THF).

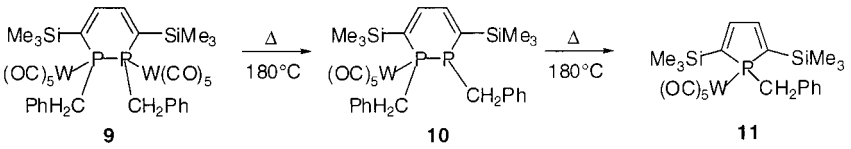
In view of the high strength of the P−O bond, complex **5** represented a dead end. Thus, we were obliged to change our strategy. Starting again from the anion **3**, we performed its benzylation giving complex **6** in acceptable yield (Scheme 2).

Complex **6** was then dealkylated as previously. The formation of the intermediate P(Bn)−P$^-$ monoanion (**7**) was monitored by ^{31}P NMR: AX system, δ_A + 19.4 (P−CH_2Ph), δ_B −102.6 (P$^-$), $^1J_{(P-P)}$ = 327 Hz. Upon protonation, it gives complex **8**, which has a characteristic ^{31}P NMR spectrum: δ (P−H) −45.3, $^1J_{(P-P)}$ = 121.8 Hz, $^1J_{(P-H)}$ = 341.3 Hz; δ (PCH_2Ph) −15.1 ($CDCl_3$). The mass spectrum of **8** (EI) shows a base peak at *m*/*z* 527, which may correspond to the η^6-1,2-diphosphinine−$W(CO)_3$ complex. However, the thermolysis of **8** under vacuum at 170−200 °C gave disappointing results. After 45 min, a complex mixture of products was obtained. The most interesting product of this mixture displays a AX ^{31}P spectrum: δ_A −56, δ_X + 295, $J_{(AX)}$ = 51 Hz. Apparently, this reactive molecule contains one dicoordinate and one tricoordinate phosphorus atom and no P−P bond. This suggests that the reaction pathway does not involve the anticipated aromatization with loss of toluene, but a 6π-cycloreversion creating two sp^2-P centers, followed by a 4π-electrocyclization retransforming one of the sp^2-centers into an sp^3-phosphorus.[10] After filtration through Florisil in hexane, this species disappeared. The ^{31}P NMR spectrum of the filtrate shows singlets at +147.8, +120.8, and −86.7, plus a new AX system: δ_A −81, δ_X −127, $^1J_{(AX)}$ = 146.7 Hz, corresponding to a P−P bonded species. The mass spectrum is very similar to that of **8**, except that the *m*/*z* 527 peak almost disappears.

To get more reliable information on the thermal evolution of these 1,2-dihydro-1,2-diphosphinine complexes, we transformed the monoanion **7** into the 1,2-dibenzyl derivative **9**. The thermolysis of **9** proved to be cleaner than that of **8**. After 8 min, the monitoring

(10) 1-Phosphadiene complexes are known to cyclize readily: Tran Huy, N. H.; Ricard, L.; Mathey, F. *Organometallics* **1988**, *7*, 1791.

Scheme 3



of the reaction mixture by ^{31}P NMR showed the complete transformation of **9** into the monocomplex **10**: δ (P−W) −21.8, $^{1}J_{(P-W)}$ = 230 Hz, $^{1}J_{(P-P)}$ = 282.7 Hz; δ (P−Bn) −79.0. Further heating led to a single compound with a ^{31}P resonance at +46.0 ($CDCl_3$). A detailed analysis demonstrated that this compound was the phosphole complex **11**. Both the ^{1}H and ^{13}C NMR spectra demonstrate that the molecule is symmetrical, and the mass spectrum indicates that one (Bn−P−$W(CO)_5$) unit has been lost. The reactions are depicted in Scheme 3. It is tempting to propose as a first step of this ring contraction a 6π-electrocyclic ring-opening followed by a loss of benzylphosphinidene and a recyclization.

What can we conclude from this series of experiments concerning the stability of 1,2-diphosphinines? It must be stressed that we have used bulky [3,6-($Me_3Si)_2$] substitution and P−$W(CO)_5$ complexation, which are both known to provide kinetic stability to the P=P double bond. Besides, the thermolytic approach is especially adapted to the synthesis of highly reactive molecules. Thus our negative results cannot be dismissed easily. We think that a low-energy pathway probably allows the aromatic 1,2-diphosphinines to evolve toward more stable products.

Experimental Section

All reactions were performed under an inert atmosphere (nitrogen or argon). NMR spectra were measured on a Bruker 300 MHz multinuclear spectrometer. Chemical shifts are expressed in ppm from internal TMS (^{1}H and ^{13}C) or external 85% H_3PO_4(^{31}P); coupling constants are expressed in Hz. Mass spectra (electron impact, unless otherwise noted) were measured at 70 eV by the direct inlet method. Elemental analyses were performed at the Service de Microanalyse du CNRS, Gif sur Yvette, France.

[1-(2-Ethoxycarbonylethyl)-2-trimethylsilylphosphirene]pentacarbonyltungsten (1). A solution of the 7-phosphanorbornadiene precursor[11] (5 g, 7.4 mmol) and an excess of trimethylsilylacetylene (ca. 2.5 mL) in toluene (25 mL) was refluxed at 110 °C for 20 h. After evaporation of the solvent, the residue was chromatographed on silica gel with 5:3 hexane/CH_2Cl_2 as the eluent. Phosphirene **1** was isolated as an oil (2.5 g, 62%). ^{31}P NMR (1:1 CH_2Cl_2/hexane): δ −175.3, $^{1}J_{(P-W)}$ = 272 Hz. ^{1}H NMR ($CDCl_3$): δ 0.29 (s, $SiMe_3$), 1.22 (t, CH_3-(Et)), 1.88 (*A*BX, 1H, CH_2), 2.10 (A*B*X, 1H, CH_2), 4.10 (q, OCH_2), 8.82 (d, $^{2}J_{(H-P)}$ = 25.2 Hz, ring H). ^{13}C NMR ($CDCl_3$): δ −1.36 (s, $SiMe_3$), 14.38 (s, CH_3(Et)), 30.31 (d, $J_{(C-P)}$ = 2.5 Hz, CH_2), 32.61 (d, $J_{(C-P)}$ = 3.3 Hz, CH_2), 141.71 (d, $^{1}J_{(C-P)}$ = 16.8 Hz, ring CH), 144.68 (d, $^{1}J_{(C-P)}$ = 37.0 Hz, ring C), 171.85 (d, $^{3}J_{(C-P)}$ = 9.9 Hz, CO_2), 196.40 (d, $^{2}J_{(C-P)}$ = 8.2 Hz, *cis*-CO), 198.50 (d, $^{2}J_{(C-P)}$ = 30.6 Hz, *trans*-CO). MS (^{184}W): *m*/*z* 554 (M^+, 11%), 526 (M^+ − 2CO, 27%), 414 (M^+ − 5CO, 100%). Anal. Calcd for $C_{15}H_{19}O_7PsiW$: C, 32.51; H, 3.46. Found: C, 32.85; H, 3.51.

[1,2-Bis(2-ethoxycarbonylethyl)-3,6-bis(trimethylsilyl)-1,2-dihydro-1,2-diphosphinine]decacarbonylditungsten (2). A solution of complex **1** (2 g, 3 mmol) and [$Pd(PPh_3)_4$] (50 mg) in toluene (20 mL) was heated at 85 °C overnight. After evaporation, the residue was chromatographed with 1:1 hexane/CH_2Cl_2 as the eluent. Complex **2** was isolated as yellow crystals (1.2 g, 70%). ^{31}P NMR ($CDCl_3$): δ 2.6. ^{1}H NMR ($CDCl_3$): δ 0.35 (s, $SiMe_3$), 1.25 (t, CH_3(Et)), 2.45, 2.70 (m, CH_2), 4.17 (q, OCH_2), 6.74 (pseudo t, $\sum J_{(H-P)}$ = 30.2 Hz, ring CH). ^{13}C NMR ($CDCl_3$): δ 1.64 (s, $SiMe_3$), 14.36 (s, CH_3(Et)), 26.01-(pseudo t, $\sum J_{(C-P)}$ = 34.8 Hz, CH_2P), 31.83 (pseudo t, $\sum J_{(C-P)}$ = 8.9 Hz, *C*H_2CO), 61.76 (s, OCH_2), 138.22 (s, *C*-$SiMe_3$), 142.94 (pseudo t, $\sum J_{(C-P)}$ = 15.5 Hz, ring CH), 171.05 (pseudo t, $\sum J_{(C-P)}$ = 19.9 Hz, CO_2), 196.60 (m, *cis* CO). MS: *m*/*z* 829 (M^+ − 10CO + H, 4%), 543 (100%). Anal. Calcd for $C_{30}H_{38}O_{14}P_2Si_2W_2$: C, 32.51; H, 3.46. Found: C, 32.84; H, 3.62.

[1-Chloro-2-(2-ethoxycarbonylethyl)-3,6-bis(trimethylsilyl)-1,2-dihydro-1,2-diphosphinine]decacarbonylditungsten (4). Potassium *tert*-butoxide (0.1 g, 0.9 mmol) was added to a solution of complex **2** (1 g, 0.9 mmol) in THF (10 mL) at room temperature. The solution turned deep red, and the formation of the anion **3** was monitored by ^{31}P NMR. Then the solution was cooled to −50 °C, and a solution of tosyl chloride (0.17 g, 0.9 mmol) in THF (3 mL) was added dropwise. After stirring at room temperature, the solution was concentrated and the residue chromatographed with 1:1 hexane/CH_2Cl_2 as the eluent. Complex **4** was thus isolated (0.72 g, 77%). ^{31}P NMR ($CDCl_3$): δ 22.2 and 107.1, $^{1}J_{(P-P)}$ = 172 Hz. ^{1}H NMR ($CDCl_3$): δ 0.34 (d, $^{4}J_{(H-P)}$ = 2.4 Hz, $SiMe_3$), 0.38 (d, $^{4}J_{(H-P)}$ = 5.1 Hz, $SiMe_3$), 1.26 (t, CH_3(Et)), 2.5−3.2 (m, CH_2), 4.18 (q, OCH_2), 6.66 (ABXY, ring CH). ^{13}C NMR ($CDCl_3$): δ 1.15 (s, $SiMe_3$), 1.58 (s, $SiMe_3$), 14.35 (s, CH_3(Et)), 25.40 (dd, $^{1}J_{(C-P)}$ = 23.4 Hz, $^{2}J_{(C-P)}$ = 10.3 Hz, CH_2P), 30.35 (d, $^{2}J_{(C-P)}$ = 6.6 Hz, *C*H_2CO), 61.61 (s, OCH_2), 140.35 (s, *C*-$SiMe_3$), 140.89 (d, $^{2}J_{(C-P)}$ = 16.5 Hz, ring CH), 142.38 (d, $^{2}J_{(C-P)}$ = 21.3 Hz, ring CH), 143.35 (d, $^{1}J_{(C-P)}$ = 10.9 Hz, *C*-$SiMe_3$), 171.24 (d, $^{3}J_{(C-P)}$ = 20.5 Hz, CO_2), 195.95 (d, $^{2}J_{(C-P)}$ = 6.4 Hz, *cis*-CO), 196.46 (d, $^{2}J_{(C-P)}$ = 6.0 Hz, *cis*-CO). MS: *m*/*z* 903 (M^+ − 5CO) 6%), 543 (100%).

[1-Hydroxy-3,6-bis(trimethylsilyl)-1,2-dihydro-1,2-diphosphinine]decacarbonylditungsten (5). Potassium *tert*-butoxide (0.13 g, 1.2 mmol) was added to a solution of complex **4** (0.63 g, 0.6 mmol) in THF (5 mL) at room temperature. The red solution was then hydrolyzed with 3 N HCl at −50 °C. After evaporation of the solvent, the product was chromatographed with 1:1 hexane/CH_2Cl_2 as the eluent. Complex **5** was isolated as a white powder (0.3 g, 54%). ^{31}P NMR (THF): δ −32.7, $^{1}J_{(P-P)}$ = 124.9 Hz, $^{1}J_{(P-H)}$ = 344.8 Hz, (PH), 84.7 (P−OH). ^{1}H NMR ($CDCl_3$): δ −0.25 (s, $SiMe_3$), 0.20 (s, $SiMe_3$), 4.3 (br, OH), 5.53 (dd, $^{1}J_{(H-P)}$ = 343.5 Hz, $^{2}J_{(H-P)}$ = 19.7 Hz, PH), 6.5 and 6.8 (2m, CH ring). ^{13}C NMR ($CDCl_3$): δ −0.66 (s, $SiMe_3$), 0.66 (s, $SiMe_3$), 133.38 (s, *C*-$SiMe_3$), 140.84 (d, $^{2}J_{(C-P)}$ = 16.5 Hz, ring CH), 142.86 (m, *C*-$SiMe_3$ + ring CH), 195.96 (d, $^{2}J_{(C-P)}$ = 6.3 Hz, *cis*-CO), 196.31 (d, $^{2}J_{(C-P)}$ = 6.5 Hz, *cis*-CO), MS: *m*/*z* 927 (M^+ + 3H, 18%), 700 (M^+ − 8CO, 73%), 459 (100%). Anal. Calcd for $C_{20}H_{22}O_{11}P_2Si_2W_2$: C, 25.99; H, 2.40. Found: C, 25.24; H, 2.54.

[1-Benzyl-2-(2-ethoxycarbonylethyl)-3,6-bis(trimethylsilyl)-1,2-dihydro-1,2-diphosphinine]decacarbonylditungsten (6). Anion **3** was formed as indicated in the synthesis of **4**. An excess of $PhCH_2Br$ was added at −20 °C, and the solution was stirred at room temperature for 1 h. The product was purified by chromatography with 1:1 hexane/CH_2Cl_2 as the eluent. Complex **6** was isolated as a yellow powder (0.4 g, 46%). ^{31}P NMR ($CDCl_3$): δ 3.7 and 12.1, $^{1}J_{(P-P)}$ = 152 Hz. ^{1}H NMR ($CDCl_3$): δ 0.33 (s, $SiMe_3$), 0.42 (s, $SiMe_3$), 1.19

(11) Espinosa-Ferao, A.; Deschamps, B.; Mathey, F. *Bull. Soc. Chim. Fr.* **1993**, *130*, 695.

(t, CH_3(Et)), 1.8−2.6 (m, CH_2CH_2), 3.6−4.15 (m, CH_2Ph + OCH_2), 6.73 (m, ring CH), 7.33 (m, Ph). ^{13}C NMR ($CDCl_3$): δ 1.54 and 1.59 (2s, $SiMe_3$), 14.08 (s, CH_3(Et)), 24.93 (dd, $J_{(C-P)}$ = 23.3 and 10.3 Hz, CH_2P), 31.73 (s, CH_2CO), 36.09 (m, CH_2-Ph), 61.06 (s, OCH_2), 128.51(s)−129.36(s)−130.83(d)−133.00-(s) (Ph), 137.82 (s, $CSiMe_3$), 140.20 (s, $CSiMe_3$), 142.30 (d, $^2J_{(C-P)}$ = 18.4 Hz, ring CH), 142.87 (d, $^2J_{(C-P)}$ =18.6 Hz, ring CH), 196.66 (d, $^2J_{(C-P)}$ = 5.9 Hz, *cis*-CO), 196.86 (d, $^2J_{(C-P)}$ = 5.8 Hz, *cis*-CO). Anal. Calcd for $C_{32}H_{36}O_{12}PSi_2W_2$: C, 34.99; H, 3.30. Found: C, 34.91; H, 3.25.

[1-Benzyl-3,6-bis(trimethylsilyl)-1,2-dihydro-1,2-diphosphinine]decacarbonylditungsten (8). Potassium *tert*-butoxide (90 mg, 0.8 mmol) was added to a solution of complex **6** (0.4 g, 0.4 mmol) in THF (5 mL). The solution turned deep red. After a few minutes, the solution was hydrolyzed by 3 N HCl at −50 °C. The product was purified by chromatography with 2:1 hexane/CH_2Cl_2 as the eluent. Complex **8** was isolated as a yellow powder (0.25 g, 63%). ^{31}P NMR ($CDCl_3$): δ −45.3, $^1J_{(P-P)}$ = 122 Hz, $^1J_{(P-H)}$ = 341 Hz (PH); −15.1 (PCH_2Ph). ^{1}H NMR ($CDCl_3$): δ 0.34 (s, $SiMe_3$), 0.42 (s, $SiMe_3$), 3.50 (m, 1H, CH_2Ph), 4.26 (m, 1H, CH_2Ph), 5.52 (dd, $^1J_{(H-P)}$ = 341 Hz, $^2J_{(H-P)}$ = 17.5 Hz, PH), 6.86 (m, 2H, ring CH). ^{13}C NMR ($CDCl_3$): δ −0.47 (s, $SiMe_3$), 1.27 (s, $SiMe_3$), 36.47 (dd, $J_{(C-P)}$ = 18.6 and 7.9 Hz, CH_2Ph), 128.24(s)−129.47(s)−130.21(d)−132.97(s) (Ph), 133.97 (s, $CSiMe_3$), 135.40(s, $CSiMe_3$), 142.17 (d, $^2J_{(C-P)}$ = 21.2 Hz, ring CH), 143.61 (d, $^2J_{(C-P)}$ = 23.3 Hz, ring CH), 195.90 (d, $^2J_{(C-P)}$ = 5.8 Hz, *cis*-CO), 196.13 (d, $^2J_{(C-P)}$ = 6.3 Hz, *cis*-CO). MS: *m*/*z* 1000 (M^+ + 2H, 13%), 527 (100%). Anal. Calcd for $C_{27}H_{28}O_{10}P_2Si_2W_2$: C, 32.48; H, 2.83. Found: C, 32.68; H, 2.83.

Thermolysis of Complex 9. The preparation of complex **9** from anion **7** was similar to that of complex **6** from anion **3**. Complex **9**: ^{31}P NMR ($CDCl_3$): δ 20.6. ^{1}H NMR ($CDCl_3$): δ 0.41 (s, $SiMe_3$), 3.81 (m, CH_2Ph), 6.80 (pseudo t, $\sum J_{(H-P)}$ = 28.6 Hz, ring CH), 7.16 (m, Ph ortho), 7.26 (m, Ph). ^{13}C NMR ($CDCl_3$): δ 0.0 (s, $SiMe_3$), 34.09 (m, CH_2Ph), 137.61 (s, $CSiMe_3$), 141.02 (pseudo t, $\sum J_{(C-P)}$ = 14.6 Hz, ring CH), 195.08 (m, *cis*-CO). MS: *m*/*z* 1007 (M^+ − 3 CO + H, 2.3%), 810 (M^+ − 10 CO, 4.4%), 534 (M^+ − 10 CO − W − $PhCH_3$, 67%), 91 ($PhCH_2$, 100%). Anal. Calcd for $C_{34}H_{34}O_{10}P_2Si_2W_2$: C, 37.52; H, 3.15. Found: C, 37.46; H, 3.19.

[1-Benzyl-2,5-bis(trimethylsilyl)phosphole]pentacarbonyltungsten (11). Complex **9** was thermolyzed in a Kugelrohr apparatus under 10^{-2} Torr at 180−200 °C. The resulting product was purified by chromatography with 4:1 hexane/CH_2Cl_2. ^{31}P NMR ($CDCl_3$): δ 46.0, $^1J_{(P-W)}$ = 206 Hz. ^{1}H NMR ($CDCl_3$): δ 0.23 (s, $SiMe_3$), 3.64 (d, $^2J_{(H-P)}$ = 5.1 Hz, CH_2Ph), 6.85 (m, 2H, Ph), 7.08 (d, $^3J_{(H-P)}$ = 35.5 Hz, ring CH), 7.15 (m, 3H, Ph). ^{13}C NMR ($CDCl_3$): δ −0.36 (s, $SiMe_3$), 36.73 (d, $^1J_{(C-P)}$ = 21 Hz, CH_2Ph), 126.79(d)−127.56(d)−128.04(d) (CH(Ph)), 135.55 (d, $^2J_{(C-P)}$ = 9.5 Hz, ipso C(Ph), 147.44 (d, $^2J_{(C-P)}$ = 10.7 Hz, Cβ), 155.71 (s, Cα), 196.84 (d, $^2J_{(C-P)}$ = 6.1 Hz, *cis*-CO), 197.58 (d, $^2J_{(C-P)}$ = 18 Hz, *trans*-CO). MS: *m*/*z* 644 (M^+ + 2H, 22%), 438 (100%). Anal. Calcd for $C_{22}H_{27}O_5PSi_2W$: C, 41.13; H, 4.24. Found: C, 41.03; H, 4.25.

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