has also been observed in another crystalline modification[36] obtained from different solvent solutions, which demonstrates that it does represent one of the minimum energy conformations available to this cyclic system.

The results of the conformational analysis in solution by NMR spectroscopy indicate that, provided one choses the right environment, solid-state and solution conformations are essentially identical, in spite of the great tendency of this cyclic molecule to exist in several quasi-isoenergetic conformations. This tendency is favored by the intrinsic flexibility, linked to the cis-trans isomerism of the two Xxx-Pro bonds, and by polar solvents that can divert one or more NH's from the formation of intramolecular hydrogen bonds.

(36) Neela, B. S.; Maujula, M. V.; Ramakumar, S.; Balasubramanian, D.; Viswamitra, M. A. *Biopolymers*, in press.

**Registry No.** CLA, 33302-55-5; CLA·2$Me_2CHOH·H_2O$, 122382-81-4.

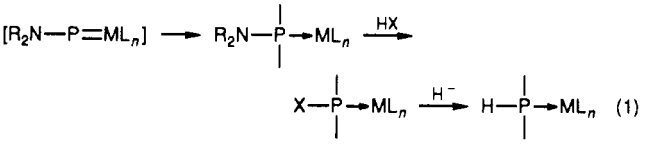
# Terminal Aminophosphinidene Complexes. A New Approach

**François Mercier, Bernard Deschamps, and François Mathey***

*Contribution from the Laboratoire de Chimie du Phosphore et des Mêtaux de Transition, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France.* *Received March 15, 1989*

**Abstract:** The thermal decomposition of [1-(diethylamino)-2,3-diphenylphosphirene]pentacarbonyltungsten at ca. 130 °C provides an access to transient [(diethylamino)phosphinidene]pentacarbonyltungsten [$Et_2N$—P=$W(CO)_5$]. This transient phosphinidene complex is trapped by 2,3-dimethylbutadiene, ethanol, and diethylamine to give the expected adducts. Similarly, [1-(diethylamino)phosphirane]pentacarbonyltungsten yields the same phosphinidene complex above 50 °C. In that case, the trapping experiments have been carried out with phenylacetylene, tolan, 2,3-dimethylbutadiene, and 1-hexene. Neither 1-alkyl- nor 1-arylphosphirene and -phosphirane P–$W(CO)_5$ complexes are efficient precursors of terminal phosphinidene complexes. The reason why 1-amino substituents so much improve the situation is thought to be the stabilization of the first singlet state of terminal aminophosphinidene complexes [$R_2N$—P=$W(CO)_5$] by comparison with their alkyl or aryl counterparts. The reaction of [1-(diethylamino)phosphirane]pentacarbonyltungsten with HCl yields the corresponding 1-chlorophosphirane complex. This complex in turn can be used as a precursor for (chlorophosphinidene)pentacarbonyltungsten [ClP=$W(CO)_5$] above 100 °C.

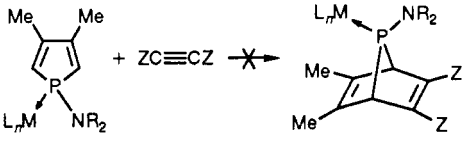
As carbene complexes $R_2C{=}ML_n$ (Fischer and Schrock types), terminal phosphinidene complexes $RP{=}ML_n$ can be divided into two subclasses according to their electrophilicity or their nucleophilicity. The electrophilic type can be viewed as a metallophosphenium cation $RP^+–M^-L_n$ and its chemistry resembles that of electrophilic carbenes.[1] The nucleophilic type is polarized in the opposite direction $R^{\delta-}P{=}M^{\delta+}L_n$ and is synthetically equivalent to $RP^{2-}$. Recently, Lappert[2] has described stable examples of the nucleophilic type. On the contrary, until now, no stable example of the electrophilic type has been reported in the literature. A priori, stabilization could be achieved with bulky substituents and reduced electrophilicity. Meeting such criteria, bulky aminophosphinidene complexes appear as a promising solution. Two results from the literature strengthen this opinion. Cowley[3] has shown that it is possible to stabilize an electrophilic phosphinidene $Fe(CO)_4$ complex by self-complexation with an internal tertiary amino group. Besides, Gladysz and Bertrand[4] have detected a bulky cationic [(diisopropylamino)phosphinidene]iron complex at low temperature by $^{31}P$ NMR. This species collapses via the insertion of phosphorus into one of the C–H bonds of the diisopropylamino group when raising the temperature. A more thorough study of terminal aminophosphinidene complexes appears all the more interesting since, as synthetic tools, they can be viewed as equivalent to masked halogenophosphinidene or unsubstituted phosphinidene complexes via a series of classical transformations carried out on the end products resulting from their chemistry (eq 1).



(1)

## Results and Discussion

The now classical route to terminal phosphinidene complexes using 7-phosphanorbornadiene complexes as precursors[1] is of no use in the case of aminophosphinidene complexes because side reactions take place between the P–N bond and dimethyl acetylenedicarboxylate (eq 2). We thus turned our attention toward



(2)

Z = $CO_2Me$

(1) This chemistry has been described in a recent review: Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275. Another recent review deals more with theoretical aspects: Cowley, A. H.; Barron, A. R. *Acc. Chem. Res.* **1988**, *21*, 81. Since the appearance of these two reviews, several new developments have been reported concerning the insertion into 3-membered rings, the reaction with carbene and carbyne complexes, the insertion into clusters, and the exchange of substituents; see: Marinetti, A.; Mathey, F. *Organometallics* **1987**, *6*, 2189. Tran Huy, N. H.; Ricard, L.; Mathey, F. *Organometallics* **1988**, *7*, 1791. Tran Huy, N. H.; Fischer, J.; Mathey, F. *Organometallics* **1988**, *7*, 240. de Vaumas, R.; Marinetti, A.; Mathey, F.; Ricard, L. *J. Chem. Soc., Chem. Commun.* **1988**, 1325. Holand, S.; Mathey, F. *Organometallics* **1988**, *7*, 1796. On the other hand, a kinetic study of the reactions of [PhP=$W(CO)_5$] with a series of para-substituted styrenes has shown that it behaves as a mild electrophile somewhat similar to a vinylidenecarbene; see: Lammertsma, K.; Chand, P.; Yang, S.-W.; Hung, J.-Te *Organometallics* **1988**, *7*, 1875.

(2) Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282.

(3) Cowley, A. H.; Geerts, R. L.; Nunn, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 6523.

(4) Nakazawa, H.; Buhro, W. E.; Bertrand, G.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 3431.

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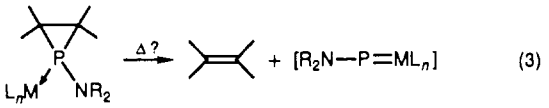
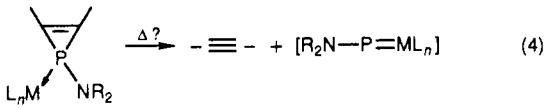
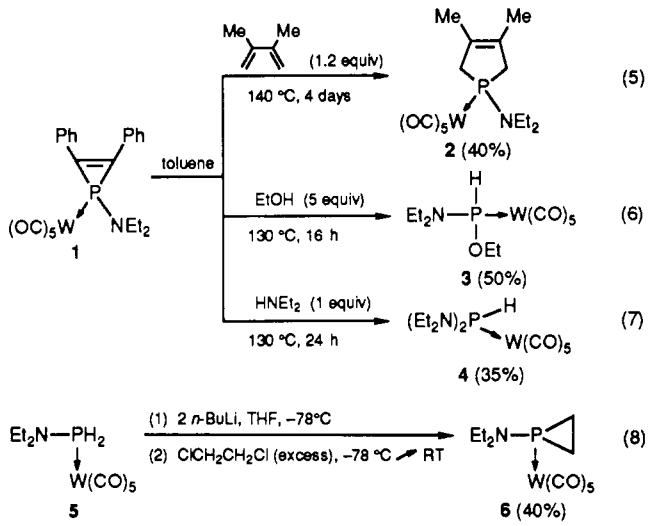
3-membered phosphirane and phosphirene rings as potential precursors (eq 3 and 4).



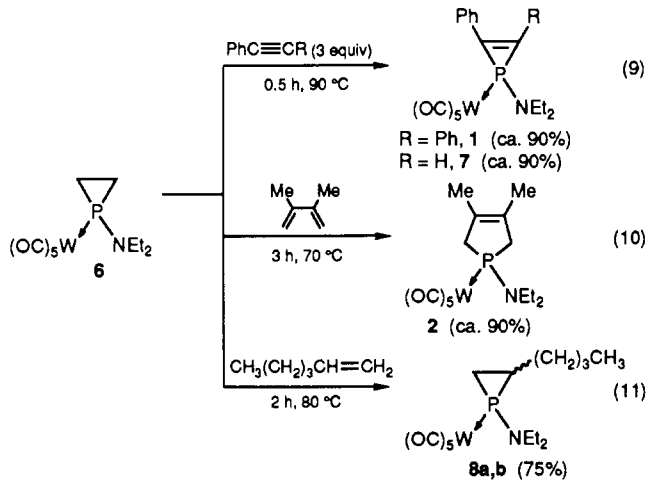




Indeed, several examples of limited generality are found in the literature concerning the use of phosphirane derivatives as precursors of transient phosphorus species such as [*t*-Bu—P=O][5] and [$(Me_3Si)_2N$—P].[6] The problem is that, as terminal phosphinidene complex precursors, phosphirane and phosphirene complexes are generally too stable to be useful.[7] However, when we thought more in depth about this problem, it appeared that the replacement of a hydrocarbon by an amino substituent in terminal phosphinidene complexes might improve the situation. The decompositions depicted in eq 3 and 4 are symmetry-allowed[8] and, hence, easier and more competitive with other decomposition paths if the terminal phosphinidene complexes have low-energy singlet states.[9] On the other hand, the nitrogen lone pair of a terminal aminophosphinidene complex more efficiently stabilizes a singlet than a triplet state (the n(N)–LUMO(P) 2e stabilizing interaction is replaced by a less efficient n(N)–SOMO(P) 3e interaction).[10] In order to check this idea, we first investigated the thermal decomposition of the already known 1-aminophosphirene P–$W(CO)_5$ complexes.[11] It must be noted here that, with a phenyl P-substituent, the decomposition takes place at ca. 160 °C and gives rise to a 4-membered ring.[12] A first positive indication came from the inspection of the mass spectrum of one such aminophosphirene complex **1**. The following comparative data are significant. $(Ph_2C_2PR)W(CO)_5$ (EI, 70 eV, $^{184}W$): R = Ph, *m/z* 610 ($M^+$, 34%), 470 (M – 5 CO, 100%), 432 (RP=$W(CO)_5$, 0%), 404 (RP=$W(CO)_4$, 17%); R = $Et_2N$ (**1**), *m/z* 605 ($M^+$, 13%), 465 (M – 5 CO, 19%), 427 (RP=$W(CO)_5$, 53%), 399 (RP=$W(CO)_4$, 100%). This comparison prompted us to investigate the reaction of [2,3-diphenyl-1-(diethylamino)phosphirene]pentacarbonyltungsten (**1**) with a series of phosphinidene trapping reagents. The results are summarized in eq 5–7.

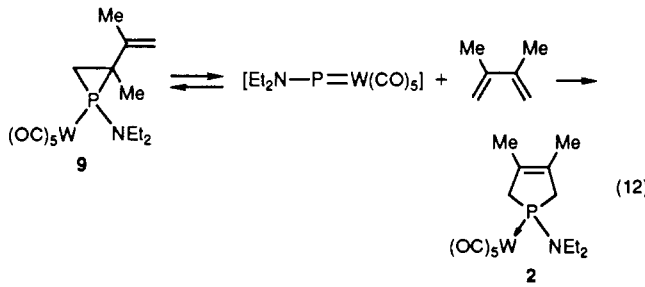
Even though the working conditions (several hours at 130–140 °C) are rather drastic, these results convincingly demonstrate that **1** can be used as a terminal phosphinidene complex precursor contrary to 1-aryl- or 1-alkylphosphirene complexes. Since phosphirane complexes are more labile than phosphirene complexes,[7] the next logical step was to synthesize a 1-aminophosphirane complex. Such a complex **6** was synthesized from the primary aminophosphine complex **5**[13] according to the route depicted in eq 8.




In order to check our hypothesis, we then studied the reactions of **6** with a series of terminal phosphinidene complex trapping reagents. The results are reported in eq 9–11.



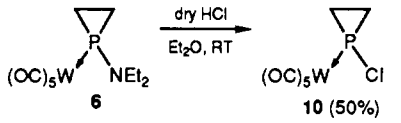

They clearly establish that **6** is a very efficient terminal aminophosphinidene complex precursor. The decomposition of **6** starts above 50 °C and the elimination of ethylene serves as a driving force in the reaction with other olefins (eq 11). Significantly, the reaction of **6** with 2,3-dimethylbutadiene directly gives the [1 + 4] adduct **2** at 70 °C. Under similar conditions, the reaction of [PhP=$W(CO)_5$] with the same diene affords the vinylphosphirane [1 + 2] adduct.[14] This probably means that the kinetic [1 + 2] adduct **9** is in equilibrium with its two components at 70 °C. Hence, the thermodynamic [1 + 4] adduct **2** becomes the only observable end product (eq 12).




The same kind of reversible dissociation explains why the two isomers of **8** [$^{31}P$ NMR ($C_6D_6$) –90.8 (major) and –92.4 (minor) ppm], which can be separated by chromatography, slowly

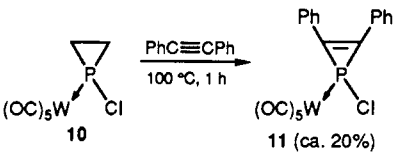
(5) Quast, H.; Heuschmann, M. *Chem. Ber.* **1982**, *115*, 901.
(6) Niecke, E.; Böske, J.; Gudat, D.; Güth, W.; Lysek, M.; Symalla, E.; *Nova Acta Leopold.* **1985**, *59*, 83.
(7) In one case, a phosphirane complex has been used as a precursor for [PhP=$W(CO)_5$] at 150 °C; see: Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134.
(8) The reaction of singlet phosphinidenes with alkenes is symmetry-allowed, and the same holds true for the reverse reaction; see: Gonbeau, D.; Pfister-Guillouzo, G. *Inorg. Chem.* **1987**, *26*, 1799.
(9) Conflicting theoretical results are available on [HP = $Cr(CO)_5$], and whether the ground state is a singlet or a triplet remains open for discussion: Gonbeau, D.; Pfister-Guillouzo, G.; Marinetti, A.; Mathey, F. *Inorg. Chem.* **1985**, *24*, 4133. Lee, J.-G.; Boggs, J. E.; Cowley, A. H. *Polyhedron* **1986**, *5*, 1027.
(10) This has been clearly demonstrated for $H_2N$–P. The separation between the first singlet excited state and the triplet ground state lies ca. 7 kcal/mol versus more than 30 kcal/mol for H–P; see: Trinquier, G. *J. Am. Chem. Soc.* **1982**, *104*, 6969.
(11) Mercier, F.; Mathey, F. *Tetrahedron Lett.* **1986**, *27*, 1323. Deschamps, B.; Mathey, F. *New J. Chem.* **1988**, *12*, 755.
(12) Marinetti, A.; Fischer, J.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 5001.
(13) Mercier, F.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1984**, 782.
(14) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.

equilibrate upon standing at room temperature. This dissociation is also the major feature of the mass spectrum of **8** (EI, 70 eV, $^{184}W$): $m/z$ 511 ($M^+$, 15%), 427 [$Et_2NPW(CO)_5$, 66%], 399 [$Et_2NPW(CO)_4$, 100%]. Complex **6** not only is a performing [(diethylamino)phosphinidene]pentacarbonyltungsten precursor but can also serve as a starting product for the synthesis of (1-chlorophosphirane)pentacarbonyltungsten (**10**, eq 13).




**6** **10** (50%) (13)

Free unsubstituted 1-chlorophosphirane is unknown at the present time, and, apparently, only 1-chlorophosphiranes with bulky substituents are stable.[15] Thus, the chemistry of complex **10** deserves some attention. It will be described in more details elsewhere. Nevertheless, in the context of this work, it must be mentioned that **10** can be used as a precursor of (chlorophosphinidene)pentacarbonyltungsten (eq 14). As such however,




**10** **11** (ca. 20%) (14)

it is far less efficient than **6** and the yield of **11** (see ref 11) remains modest.

Further developments of this program will include investigations on the various possible synthetic uses of terminal aminophosphinidene complexes. Their stabilization via the use of bulky substituents will also be studied.

## Experimental Section

All reactions were performed under argon. NMR spectra were recorded on multinuclear WP 80 SY and AC 200 SY Bruker spectrometers operating at 80.13 and 200.13 ($^1H$), 20.15 and 50.32 ($^{13}C$), and 32.44 ($^{31}P$) MHz. Chemical shifts are in ppm downfield from internal TMS ($^1H$ and $^{13}C$) and external 85% $H_3PO_4$ ($^{31}P$), and coupling constants are in hertz. Mass spectra were recorded on a Shimadzu GC–MS QP 1000 instrument at 70 eV under electronic impact. Elemental analyses were performed by the Service Central de Microanalyse du CNRS, France. Silica gel (70–230 mesh) was used for the chromatographic separations. All commercially available reagents were used as received from the suppliers.

**[1-(Diethylamino)-3,4-dimethyl-2,5-dihydrophosphole]pentacarbonyltungsten (2).** [1-(Diethylamino)-2,3-diphenylphosphirene]pentacarbonyltungsten (**1**)[11] (0.89 g, 1.47 × $10^{-3}$ mol) and 2,3-dimethylbutadiene (0.15 g, 1.76 × $10^{-3}$ mol) in 2 mL of toluene were heated at 140 °C in a sealed tube during 4 days. After cooling and evaporation of toluene, the crude reaction mixture was chromatographed with 90/10 hexane/toluene as eluent. Yield of **2**: 0.29 g (40%). $^{31}P$ NMR (toluene): $\delta$ 67.6 ($^1J(^{31}P-^{183}W)$ = 254 Hz). $^1H$ NMR ($C_6D_6$): $\delta$ 0.79 (t, $^3J$(H–H) = 7 Hz, 6 H, $CH_3CH_2$), 1.42 (d, $^4J$(H–P) = 0.6 Hz, 6 H, $CH_3C$=), 2.57 (br s, 4 H, $CH_2P$), 2.62–2.78 (m, 4 H, $CH_2N$). $^{13}C$ NMR ($C_6D_6$): $\delta$ 14.76 (d, $^3J$(C–P) = 2.4 Hz, $CH_3CH_2$), 15.64 (d, $^3J$(C–P) = 8.7 Hz, $CH_3C$=), 43.01 (d, $^2J$(C–P) = 4.9 Hz, $CH_2N$), 46.16 (d, $^1J$(C–P) = 28.6 Hz, $CH_2P$). MS ($^{184}W$): $m/z$ 509 ($M^+$, 28%), 425 (M – 3 CO, 30%), 393 (100%). Exact mass ($^{186}W$): found, 511.0631; calcd, 511.0620. Complex **2** was also obtained in 90% yield by heating **6** (0.45 g, $10^{-3}$ mol) with 1 mL of 2,3-dimethylbutadiene at 70 °C for 3 h.

**[(Diethylamino)ethoxyphosphane]pentacarbonyltungsten (3).** Complex **1** (1 g, 1.65 × $10^{-3}$ mol) and ethanol (0.38 g, 8.3 × $10^{-3}$ mol) in 2 mL of toluene were heated at 130 °C in a sealed tube during 16 h. After cooling and evaporation of toluene, the crude reaction mixture was chromatographed with 90/10 hexane/toluene as eluent. Yield of **3**: 0.4 g (50%). $^{31}P$ NMR (toluene): $\delta$ 111 ($^1J(^{31}P-^{183}W)$ = 302.7 Hz, $^1J$(P–H) = 385.7 Hz). $^1H$ NMR ($C_6D_6$): $\delta$ 0.82 [t, $^3J$(H–H) = 7.3 Hz, 6 H, $CH_3(Et_2N)$], 0.97 [t, $^3J$(H–H) = 6.7 Hz, 3 H, $CH_3(EtO)$], 2.6–3.5 (m, 6 H, $CH_2N$ + $CH_2O$), 7.35 (d, $^1J$(H–P) = 385.4 Hz, 1 H, H–P). $^{13}C$ NMR ($C_6D_6$): $\delta$ 14.69 (s, $CH_3CH_2N$), 16.07 (d, $^3J$(C–P) = 6.4 Hz, $CH_3CH_2O$), 45.41 (d, $^2J$(C–P) = 3.4 Hz, $CH_2N$), 65.85 (d, $^2J$(C–P) = 10.8 Hz, $CH_2O$), 196.66 (d, $^2J$(C–P) = 8.6 Hz, *cis*-CO), 199.80 (d, $^2J$(C–P) = 27.2 Hz, *trans*-CO). The compound is very unstable and does not give reliable analytical results.

**[Bis(diethylamino)phosphane]pentacarbonyltungsten (4).**[11] Complex **1** (0.79 g, 1.31 × $10^{-3}$ mol) and diethylamine (0.1 g, 1.37 × $10^{-3}$ mol) in 2 mL of toluene were heated at 130 °C in a sealed tube for 24 h. After the usual workup, the yield of **4** was 0.26 g (35%).

**[1-(Diethylamino)phosphirane]pentacarbonyltungsten (6).** The metalation of *N,N*-diethylphosphinamide complex **5**[13] (2.15 g, 5 × $10^{-3}$ mol) in 50 mL of THF was carried out by a rapid addition of 6.6 mL of *n*-BuLi (1.5 M in hexane, $10^{-2}$ mol) at −78 °C. Just after the end of the addition of *n*-BuLi, an excess of 1,2-dichloroethane (1 mL, 1.3 × $10^{-2}$ mol) was directly added. Then, the resulting mixture was allowed to warm up to room temperature and stirred 1 h more at this temperature. This solution was extracted with $Et_2O$ (100 mL), washed twice (10 mL) with water, dried on $Na_2SO_4$, filtered, evaporated, and chromatographed on silica gel, **6** being obtained with hexane/toluene (50/50). The procedure gave 0.9 g of a yellow oil (yield 40%) of **6**, which was fully characterized. $^{31}P$ NMR ($CDCl_3$): $\delta$ −111.0 ($^1J(^{31}P-^{183}W)$ = 278 Hz. $^1H$ NMR ($CDCl_3$): $\delta$ 1.12 (t, $^3J$(H–H) = 7.3 Hz, 6 H, $CH_3CH_2$), 1.45–1.66 (m, 4 H, $CH_2$), 2.75 (dq, $^3J$(H–P) = 12.4 Hz, 4 H, $CH_2N$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 13.36 (d, $^1J$(C–P) = 14.65 Hz, $CH_2$), 14.53 (d, $^3J$(C–P) = 4.88 Hz, $CH_3CH_2$), 46.19 (d, $^2J$(C–P) = 6.1 Hz, $CH_3CH_2$), 195.98 (d, $^2J$(C–P) = 9.75 Hz *cis*-CO), 198.52 (d, $^2J$(C–P) = 31.74 Hz, *trans*-CO). MS ($^{184}W$): $m/z$ 455 ($M^+$, 8%), 427 (M – $C_2H_4$, 28%), 315 (M – (4 CO + $C_2H_4$) 100%). IR (decalin): $\nu$(CO) 2070, 1940 $cm^{-1}$. Anal. Calcd for $C_{11}H_{14}NO_5PW$: C, 29.03; H, 3.10; N, 3.08; P, 6.80; W, 40.40. Found: C, 29.42; H, 3.25; N, 2.94; P, 6.49; W, 39.91.

**[1-(Diethylamino)phosphirene]pentacarbonyltungstens 1 and 7.** Complex **6** (0.45 g, $10^{-3}$ mol) was heated with an excess of tolan (0.54 g, 3 × $10^{-3}$ mol) in 2 mL of toluene at 90 °C for 0.5 h; yield of **1** was 90% after chromatography on a short column. The same procedure with phenylacetylene gave complex **7** almost quantitatively.

**[1-(Diethylamino)-2-*n*-butylphosphirane]pentacarbonyltungsten (8a,b).** Complex **6** (0.9 g, 2 × $10^{-3}$ mol) was heated with 1-hexene (1 mL, 8 × $10^{-3}$ mol) at 80 °C for 2 h. After evaporation, the residue was chromatographed with hexane/toluene (90/10), yielding 0.75 g (75%) of a mixture of **8a,b**. The isomers **8a** and **8b** were obtained in the pure state with a second chromatography with pure hexane ($R_f$: **8a**, 0.23; **8b**, 0.30). **8a** [**8b**]: $^{31}P$ ($C_6D_6$) −90.8 $^1J(^{31}P-^{183}W)$ = 278 Hz [−92.4, $^1J(^{31}P-^{183}W)$ = 273 Hz]; $^{13}C$ ($C_6D_6$) 14.14 ($CH_3(CH_2)_3$) [13.97], 14.82 (d, $^3J$(C–P) = 3.65 Hz, $CH_3CH_2N$) [14.48], 20.65 (d, $^1J$(C–P) = 15.2 Hz, $PCH_2$) [18.55, $^1J$(C–P) = 11.8 Hz], 28.54 (d, $^1J$(C–P) = 16.1 Hz, $PCH(CH_2)$ [29.06, $^1J$(C–P) ≃ 0 Hz], 46.52 (d, $^2J$(C–P) = 5.6 Hz, $CH_2N$) [46.40, J = 7.0 Hz]. IR (decalin): $\nu$(CO) 2070, 1940 $cm^{-1}$. Anal. Calcd for $C_{15}H_{22}NO_5PW$: C, 35.25; H, 4.34; N, 2.74. Found: C, 35.09; H, 4.15; N, 2.86.

**(1-Chlorophosphirane)pentacarbonyltungsten (10).** Dried gaseous hydrogen chloride was bubbled through a solution of aminophosphirane **6** (0.9 g, 2 × $10^{-3}$ mol) in 20 mL of anhydrous $Et_2O$ for 15 min. The flask was stopped and kept at room temperature for 18 h. Removal of the solvent from the filtered solution gave crude **10** as an oil, which was chromatographed with hexane/toluene (80/20). The air-sensitive pale yellow oil thus obtained was crystallized from hexane (0.55 g, 50%). MP: 45 °C. $^{31}P$ NMR ($C_6D_6$): $\delta$ −101.3 ($^1J$ ($^{31}P-^{183}W$) = 302.7 Hz. $^1H$ NMR ($C_6D_6$): 0.33–1.19 (m, 4 H). $^{13}C$ NMR ($C_6D_6$): $\delta$ 14.27 (d, $^1J$(C–P) = 9.58 Hz, $CH_2$), 194.33 (d, $^2J$(C–P) = 8.47 Hz, *cis*-CO), 197.44 (d, $^2J$(C–P) = 44.0 Hz, *trans*-CO). MS ($^{184}W$, $^{35}Cl$): $m/z$ 418 ($M^+$, 40%), 390 (M – CO, 15%), 306 (M – 4 CO, 100%). IR ($CH_2Cl_2$): $\nu$(CO) 2078, 1950 $cm^{-1}$. Anal. Calcd for $C_7H_4ClO_5PW$: C, 20.09; H, 0.96. Found: C, 20.20; H, 1.04.

**(2,3-Diphenyl-1-chlorophosphirene)pentacarbonyltungsten (11).** Complex **7** (0.8 g, 2 × $10^{-3}$ mol) was heated with tolan (0.54 g, 3 × $10^{-3}$ mol) in 2 mL of toluene at 100 °C for 1 h. After chromatography, 0.22 g of complex **11** was obtained (20%).

**Registry No. 1**, 108809-74-1; **2**, 123307-83-5; **3**, 123307-84-6; **4**, 108809-71-8; **5**, 93493-00-6; **6**, 123307-85-7; **7**, 108809-72-9; **8a**, 123307-86-8; **8b**, 123406-54-2; **10**, 123307-87-9; **11**, 103055-90-9; $H_2C$=C(Me)C(Me)=$CH_2$, 513-81-5; $Cl(CH_2)_2Cl$, 107-06-2; PhC≡CPh, 501-65-5; $H_3C(CH_2)_3CH$=$CH_2$, 592-41-6; phenylacetylene, 536-74-3.

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