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Reaction of Terminal Phosphinidene Complexes with Aldimines: Synthesis of the First 1,2,3-Azadiphosphetidine

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ABSTRACT: *Transient terminal phosphinidene complexes [RP-M(CO)$_5$] (M = Mo, W, R = Ph, Me), as generated from the corresponding 7-phosphanorbornadiene complexes, react with N-methyl(benzylidene)amine to afford the diazaphospholane complexes* **3,4** *(R = Ph) or a mixture of diazaphospholane* **9** *and 1,2,3-azadiphosphetidine* **10** *(R = Me), probably by insertion of either one molecule of imine or one molecule of phosphinidene into the weak P–N bond of the unstable intermediate azaphosphiridine* **11.** *The new complex* **10** *has been submitted to an X-ray crystal structure analysis.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9: 597–600, 1998

INTRODUCTION

A few examples of azaphosphiridines are described in the literature, but no studies on the reactivity of these strained C-N-P three-membered ring systems have ever been published. The first λ^3-azaphosphiridine was reported by Niecke et al. and resulted from the isomerization of an imino(methylene)phosphorane [1]. Other λ^5-azaphosphiridines can be obtained by a photochemical N_2 extrusion from the corresponding λ^5-triazaphospholenes [2]. Very recently, Streubel et al. performed the synthesis of an azaphosphiridine pentacarbonyltungsten complex by thermolysis of a 2*H*-azaphosphirene tungsten complex in the presence of *N*-methyl(benzylidene)amine [3]: The intermediate terminal phosphinidene-W(CO)$_5$ complex is supposed to add to the imine either in a concerted or a stepwise manner. The final product is stabilized by the steric bulk of the substituent on the phosphorus atom. We report here that the analogous additions of unhindered electrophilic terminal phosphinidene complexes to (*E*) *N*-methyl(benzylidene)amine give rise to two different types of products, the four- and five-membered 1,2,3-azadiphosphetidines and 1,4,2-diazaphospholanes. We propose that unstable azaphosphiridine complexes are common intermediates to these two products.

RESULTS AND DISCUSSION

The phosphinidene complexes [PhP-M(CO)$_5$] were generated from the corresponding 7-phenyl-7-phosphanorbornadiene complexes **1** (M = W) and **2** (M = Mo) in the presence of CuCl as a catalyst at around 60°C [4]. Their reaction with an excess of *N*-methyl (benzylidene)amine afforded directly the 1,4,2-diazaphospholane complexes **3** and **4** in 48 and 35% yields, respectively. Despite the presence of the chiral carbon and phosphorus atoms, a single diastereoisomer was observed for **3** and **4,** but we have no reliable information on its stereochemistry (Scheme 1).

Complexes **3** and **4** were fully characterized by mass spectrometry, ^{31}P, ^{1}H, and ^{13}C NMR. The presence of the two *N*-methyls on the 1- and 4-positions

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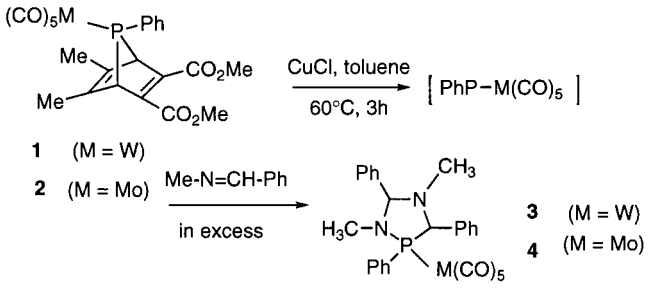
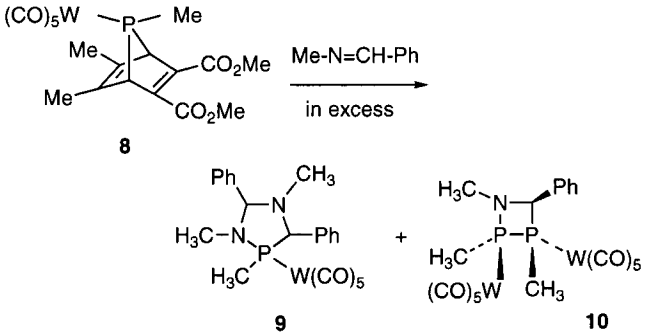


SCHEME 1



SCHEME 2

of the ring is confirmed by the ^{1}H-NMR spectra: the methyl groups appear as a doublet ($^3J_{HP}$ = 9.5 Hz) and a singlet in both cases. The two benzylic protons are also characteristic: For **3,** they appear as two doublets (J_{HP} = 5.4 and 2.5 Hz). In the ^{13}C-NMR spectra, the two benzylic carbon atoms are easily assigned, given the large difference between the $^1J_{CP}$ and $^2J_{CP}$ coupling constants (35.3 and 2.9 Hz for **3** and 30.7 and 4.0 Hz for **4**). A parallelism can be established between the observed reactivity of the transient terminal phosphinidene complexes and that of the phosphenium cations that react with aldimines, at low temperature, to afford 1,4,2-diazaphospholanium salts, as mixtures of two diastereoisomers [5]. Another approach to 1,4,2-diazaphospholane derivatives is the reaction between halogeno-alkylphosphite and aldimines, at room temperature [6]. The obtention of a single isomer of diazaphospholanes **3** and **4** can be explained by the presence of the bulky metal group on the phosphorus atom. But when the reaction was performed at 110°C, without CuCl, three other isomers of **3** (**5–7**) have been detected by ^{31}P-NMR spectroscopy (chemical shifts at around 80 ppm). They were separated by chromatography on SiO_2 and characterized by mass spectrometry, ^{31}P, ^{1}H, and ^{13}C NMR.

Under the same conditions, the 7-methyl-7-phosphanorbornadiene tungsten complex **8** reacts with an excess imine, leading to a mixture of two products: the diazaphospholane **9** (25% yield) and the 1,2,3-azadiphosphetidine **10** (17% yield). When the reaction was performed with an excess of 7-phosphanorbornadiene **8** (1.5 eq), the four-membered ring **10** was isolated as the major product in a 3:1 ratio to the five-membered ring **9** (Scheme 2).

Compound **9** was characterized by mass spectrometry, ^{31}P, ^{1}H, and ^{13}C NMR. In the ^{1}H-NMR spectrum, both CH_3 groups appear as doublets and have almost the same coupling constants with phosphorus, $^3J_{HP}$ = 11.6 Hz and $^4J_{HP}$ = 11.3 Hz; the benzylic protons are different; one appears as a doublet and the other as a singlet. The same general trends as for **3** and **4** were observed in the ^{13}C-NMR spectrum.

Complex **10** was fully characterized. It displays a characteristic ^{31}P AX spectrum: δ = 29.28 and 105.19 ppm, ΣJ_{PP} = 26.9 Hz. In the ^{1}H-NMR spectrum, the 2-Me and the 3-Me appear as doublets of doublets and the N-Me as a doublet. The ^{13}C-NMR and the mass spectra confirm the proposed structure. The stereochemistry of **10** was determined by an X-ray crystal structure analysis (Figure 1). The four-membered ring is nonplanar as shown by the P_2-C_1-N-P_1 torsion angle of 25°. Some strain is present as indicated by the very long P_2–C_1 bond at 1.887 (5) Å. The coordination of the nitrogen atom is almost planar as expected: Σ angles = 345.5°. The two $W(CO)_5$ groups are *trans,* and the phenyl lies on the same side of the ring as the vicinal *P*-methyl substituent. Complex **10** is the first 1,2,3-azadiphosphetidine reported to date. The isomeric symmetrical heterocycles (1,2,4-azadiphosphetidine) have been obtained by cyclization of diphosphinomethanes with primary amines [7]. Both complexes **9** and **10** could be formed via the same unstable intermediate, the azaphosphiridine **11** by insertion of either one molecule of imine or one molecule of phosphinidene into the weak P–N bond. We remark that the last insertion is very sensitive to steric hindrance: With the phenylphosphinidene complexes generated from **1** and **2,** no four-membered rings have been isolated (see Scheme 3).

We wish to emphasize the analogy between the reaction leading to **10** and the insertion of terminal phosphinidene complexes into alkynylphosphirene complexes [8] and other three-membered saturated heterocycles such as thiiranes, oxiranes, and aziridines [9]. This work shows, once more, the high synthetic potential of electrophilic terminal phosphinidene complexes: In a one-step reaction, we can prepare 1,2,3-azadiphosphetidines, a previously unknown structure.

EXPERIMENTAL

All reactions were performed under nitrogen; the solvents were purified, dried, and degassed by stan-

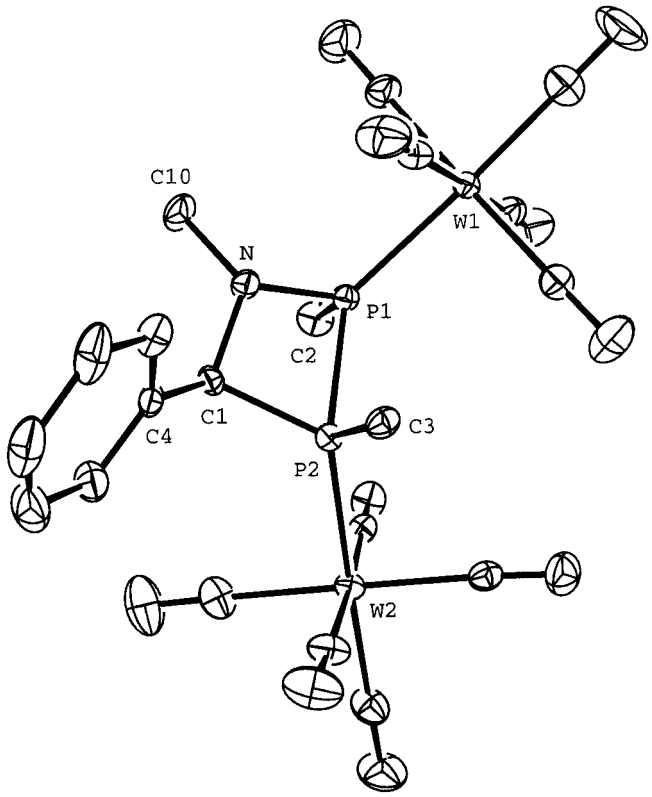
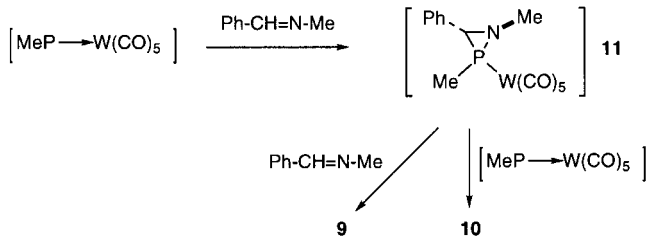


FIGURE 1 ORTEP drawing of one molecule of **10.** Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): W1-P1 2.452 (1), W2-P2 2.471 (1), P1-P2 2.237 (2), P1-N 1.717 (4), P1-C2 1.830 (6), P2-C1 1.887 (5), P2-C3 1.820 (5), C1-N 1.470 (7), C1-C4 1.508 (7), N-C10 1.456 (6); W1-P1-P2 127.71 (6), W1-P1-N 117.8 (2), W1-P1-C2 116.8 (2), P2-P1-N 77.3 (2), P2-P1-C2 103.1 (2), N-P1-C2 106.9 (2), W2-P2-P1 131.36 (6), W2-P2-C1 122.4 (2), W2-P2-C3 115.3 (2), P1-P2-C1 75.1 (2), P1-P2-C3 101.2 (2), C1-P2-C3 103.2 (2), P2-C1-N 95.6 (3), P2-C1-C4 115.9 (3), N-C1-C4 115.1 (4), P1-N-C1 104.7 (3), P1-N-C10 122.0, C1-N-C10 118.8 (4).



SCHEME 3

dard techniques. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13, 50.32, and 81.01 MHz, respectively. All chemical shifts are reported in ppm downfield from internal TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra (EI) were obtained at 70 eV by the direct inlet method.

Synthesis of [1,4-Dimethyl-2,3,5-triphenyl-1,4,2-diazaphospholane]pentacarbonyltungsten

A solution of 7-phosphanorbornadiene complex **1** (0.65 g, 1 mmol), 0.3 mL of (*E*) *N*-methyl(benzylidene)amine, and 50 mg of CuCl as a catalyst in toluene (5 mL) was heated at 60°C for 2.5 hours. After evaporation, the residue was chromatographed on silica gel (70–230 mesh Merck) with hexane/CH_2Cl_2 20/4 as the eluent: 0.30 g of complex **3** was isolated as a white powder (yield 48%). ^{31}P NMR ($CDCl_3$): δ 88.0, $^{1}J_{PW}$ = 274.7 Hz; ^{1}H NMR ($CDCl_3$): δ 1.86 (s, 3H, 4-CH_3), 2.77 (d, $^{3}J_{HP}$ = 9.5 Hz, 3H, 2-CH_3), 4.84 (d, $^{2}J_{HP}$ = 5.4 Hz, 1H, −C*H*-Ph), 5.56 (d, $^{3}J_{HP}$ = 2.5 Hz, 1H,-C*H*-Ph); ^{13}C NMR ($CDCl_3$): δ 33.56 (d, $^{3}J_{CP}$ = 6.4 Hz, N-CH_3), 35.64 (d, $^{2}J_{CP}$ = 7.7 Hz, N-CH_3), 74.06 (d, $^{1}J_{C\text{-}P}$ = 35.3 Hz, *C*H-Ph), 88.29 (d, $^{2}J_{C\text{-}P}$ = 2.9 Hz, *C*H-Ph), 197.00(d, $^{2}J_{CP}$ = 7.6 Hz, CO *cis*), 198.57 (d, $^{2}J_{CP}$ = 14.5 Hz, CO *trans*); Mass (^{184}W): *m/z* 670 (M^+, 4%), 642 (M^+-CO, 3%), 551 (M^+-PhCH = NMe, 83%), 467 (M^+-PhCH = NMe-3CO, 100%).

Synthesis of [1,4-Dimethyl-2,3,5-triphenyl-1,4,2-diazaphospholane]pentacarbonylmolybdenum **4**

A solution of 7-phosphanorbornadiene complex **2** (0.56 g, 1 mmol), 0.3 mL of (*E*) *N*-methyl(benzylidene)amine (2 g, 10 mmol), and 50 mg of CuCl in toluene (5 mL) was heated at 60°C for 2.5 hours. After evaporation, the residue was chromatographed on silica gel, with hexane/CH_2Cl_2 as the eluent: 0.20 g of **4** was isolated as a white powder (yield 35%).

^{31}P NMR ($CDCl_3$): δ 109.4; ^{1}H NMR ($CDCl_3$): δ 1.88 (s, 3H, 4-CH_3), 2.81 (d, $^{3}J_{HP}$ = 9.6 Hz, 3H, 1-CH_3), 4.80 (d, $^{2}J_{HP}$ = 6.5 Hz, 1H, C*H*-Ph), 5.55 (d, $^{3}J_{HP}$ = 1.9 Hz, 1H, C*H*-Ph); ^{13}C NMR ($CDCl_3$): δ 33.48 (d, J_{CP} = 7.6 Hz, N-CH_3), 35.70 (d, J_{CP} = 7.64 Hz, N-CH_3), 73.79 (d, $^{1}J_{CP}$ = 30.7 Hz, Ph-*C*H), 88.38 (d, $^{2}J_{CP}$ = 4.0 Hz, Ph-*C*H), 206.03 (d, $^{2}J_{CP}$ = 9.45 Hz, CO *cis*), 209.53 (d, $^{2}J_{CP}$ = 26.35 Hz, CO *trans*); mass (^{98}Mo): *m/z* 584 (M^+, 1%), 556 (M^+-CO, 6%), 500 (M^+-3 CO, 3%), 465 (M^+-PhCH = NCH_3, 63%), 437 (M^+-PhCH = NCH_3-CO, 24%), 381(M^+-PhCH = NCH_3-3CO, 100%).

Synthesis of a Mixture of the Four Isomers of [1,4-Dimethyl-2,3,5-triphenyl-1,4,2-diazaphospholane]pentacarbonyltungsten **3,5,6,7**

A solution of 7-phosphanorbornadiene complex **1** (0.65 g, 1 mmol), 0.5 mL of *N*-methyl (benzylidene)amine in toluene (5 mL) was heated at 110°C for 7 hours. The chromatography on SiO_2, with hexane/CH_2Cl_2 100/5 as the eluent afforded **5, 6, 3,** and **7** in that order: 80 mg of **5** (yield 12%). ^{31}P NMR

($CDCl_3$): δ 79.1 $^1J_{PW}$ = 267.6 Hz; ^{1}H NMR ($CDCl_3$): δ 1.97 (s, 3H, N-CH_3), 2.58 (d, $^3J_{H\text{-}P}$ = 10.7 Hz, 3H, N-CH_3), 4.29 (s, 1H, C*H*-Ph), 4.49 (d, $^2J_{HP}$ = 6.3 Hz, 1H, C*H*-Ph); ^{13}C NMR ($CDCl_3$): δ 35.39 (d, J_{CP} = 10.4 Hz, N-CH_3), 38.09 (d, J_{CP} = 7.7 Hz, N-CH_3), 79.06 (d, $^1J_{CP}$ = 32.2 Hz, *C*H-Ph), 89.41 (s, *C*H-Ph), 197.46 (d, $^2J_{CP}$ = 7.6 Hz, CO *cis*), 198.69 (d, $^2J_{CP}$ = 24.3 Hz, CO *trans*).

Mass: the same as described earlier, 30 mg of **6** (yield 5%). ^{31}P NMR ($CDCl_3$): δ 94.58, $^1J_{PW}$ = 289.2 Hz; ^{1}H NMR ($CDCl_3$): δ 2.12 (s, 3H, N-CH_3), 2.50 (d, $^3J_{HP}$ = 9.1 Hz, 3H, N-CH_3), 4.20 (d, $^2J_{HP}$ = 8.2 Hz, 1H, C*H*-Ph), 4.75 (s, 1H, C*H*-Ph); mass: the same as described earlier, 120 mg of **3** (yield 20%); 80 mg of **7** (yield 12%). ^{31}P NMR ($CDCl_3$): δ 84.1; ^{1}H NMR ($CDCl_3$): δ 1.89 (s, 3H, N-CH_3), 2.90 (d, $^3J_{HP}$ = 10.0 Hz), 4.54 (d, J_{HP} = 2.3 Hz), 4.82 (d, J_{HP} = 2.6 Hz).

Mass: the same as described earlier.

Synthesis of [1,2,3-Trimethyl-4-phenyl-1,2,3-azadiphosphetidine]decacarbonylditungsten **10** *and [1,2,4-Trimethyl-3,5-diphenyl-1,4,2-diazaphospholane]pentacarbonyltungsten* **9**

A solution of 7-phosphanorbornadiene complex **8** (0.60 g, 1 mmol), 0.4 mL of imine, and 40 mg of CuCl in toluene (5 mL) was heated at 60°C for 3 hours. After evaporation, the residue was chromatographed on silica gel, with hexane/CH_2Cl_2 10/2 as the eluent: 0.05 g of **10** was obtained as a white powder (yield 17%). ^{31}P NMR ($CDCl_3$): δ 29.28 (d, $^1J_{PP}$ = 26.87 Hz, P-3), 105.19 (d, P-2); ^{1}H NMR ($CDCl_3$): δ 1.80 (dd, J_{HP} = 11.15 and 6.29 Hz, 3H, 3-CH_3), 2.31 (dd, J_{HP} = 10.21 and 4.65 Hz, 3H, 2-CH_3), 2.44 (d, $^3J_{HP}$ = 13.69 Hz, 3H, N-CH_3), 5.38 (d, $^2J_{HP}$ = 8.86 Hz, 1H, PhC*H*); ^{13}C NMR ($CDCl_3$): δ 14.84 (dd, $^1J_{CP}$ = 15.5 Hz, $^2J_{CP}$ = 5.8 Hz, P-Me), 19.22 (d, $^1J_{CP}$ = 11.9 Hz, P-Me), 34.32 (d, $^2J_{CP}$ = 11.3 Hz, N-Me), 75.57 (d, $^1J_{CP}$ = 23.4 Hz, *C*HPh), 195.22 (d, $^2J_{CP}$ = 6.68 Hz, CO *cis*), 195.63 (d, $^2J_{CP}$ = 6.88 Hz, CO *cis*), 198.44 (d, $^2J_{CP}$ = 27.8 Hz, CO *trans*); mass: *m/z* 859 (M^+, 6%), 740 (M^+ − PhCH=NCH_3, 36%), 712 (M^+ − PhCH=NCH_3 − CO, 35%), 656 (M^+ − PhCH=NCH_3 − 3CO, 36%), 628 (M^+ − PhCH=NCH_3 − 4CO, 100%).

A 0.15 g amount of **9** was obtained as a white powder (yield 25%): ^{31}P NMR ($CDCl_3$): δ 73.1, $^1J_{PW}$ = 260.80 Hz; ^{1}H NMR ($CDCl_3$): δ 1.47 (d, $^2J_{HP}$ = 5.17 Hz, 3H, P-CH_3), 2.21 (d, $^3J_{HP}$ = 11.63 Hz, 3H, N-CH_3), 2.44 (d, $^4J_{HP}$ = 11.3 Hz, 3H, N-CH_3), 4.15 (s, 1H, C*H*-Ph), 4.30 (d, $^2J_{HP}$ = 3.64 Hz, 1H, C*H*-Ph); ^{13}C NMR ($CDCl_3$): δ 24.62 (d, $^1J_{CP}$ = 21.25 Hz, P-CH_3), 34.58 (d, $^2J_{C\text{-}P}$ = 10.56 Hz, N-CH_3), 37.98 (d, $^3J_{CP}$ = 8.7 Hz, N-CH_3), 75.37 (d, $^1J_{CP}$ = 36.5 Hz, *C*HPh), 89.79 (s, *C*HPh), 197.10 (d, $^2J_{CP}$ = 7.56 Hz, CO *cis*); mass: *m/z* 608 (M^+, 8%), 593 (M^+-CH_3, 15%), 535 (M^+-CH_3-2CO, 12%), 489 (M^+ − PhCH=NCH_3, 74%), 461 (M^+ − PhCH=NCH_3 − CO, 26%), 405 (M^+ − PhCH=N-CH_3 − 3CO, 100%).

X-ray Structure Determination for **10**

Crystals of **10,** $C_{20}H_{15}NO_{10}P_2W_2$, were grown from a pentane/CH_2Cl_2 solution of the compound. Data were collected at 123 ± 0.5 K on an Enraf Nonius CAD4 diffractometer using Mo K_α radiation (λ = 0.71073 Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf Nonius MOLEN package. The compound crystallizes in space group $P2_1/n$ (14), a = 10.263 (1) Å, b = 12.185 (2) Å, c = 21.186 (3) Å, β = 96.14 (1)°; V = 2634.3 (4.5) Å^3; Z = 4; d_{calc} = 2.166 g/cm^3; μ = 90.9 cm^{-1}; $F(000)$ = 1600. A total of 8413 unique reflexions were recorded in the range $2° < 2\theta < 60.0°$ of which 2524 were considered as unobserved [$F^2 < 3.0\sigma(F^2)$], leaving 5889 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.06. The final agreement factors were R = 0.030, R_ω = 0.041, G.O.F. = 1.02.

REFERENCES

[1] E. Niecke, A. Seyer, D. A. Wildbredt, *Angew. Chem. Int. Ed. Engl., 20,* 1981, 675.
[2] E. Niecke, J. Boske, B. Krebs, M. Dartmann, *Chem. Ber., 118,* 1985, 3227.
[3] R. Streubel, A. Ostrowski, H. Wilkens, F. Ruthe, J. Jeske, P. G. Jones, *Angew. Chem. Int. Ed. Engl., 36,* 1997, 378.
[4] A. Marinetti, F. Mathey, J. Fischer, A. Mitscher, *J. Am. Chem. Soc., 104,* 1982, 4484
[5] T. C. Kim, M. R. Mazieres, R. Wolf, M. Sanchez, *Tetrahedron Lett., 31,* 1990, 4459.
[6] (a) Z. S. Novikova, M. M. Kabachnik, N. V. Mashchenko, I. F. Lutsenko, *J. Gen. Chem. USSR, 55,* 1985, 404; (b) A. M. Kibardin, T. Kh. Gazizov, K. M. Enikeev, A. N. Pudovik, *Bull. Acad. Sci. USSR Div. Chem. Sci., 32,* 1983, 390.
[7] (a) Z. S. Novikova, M. M. Kabachnick, E. A. Monin, I. F. Lutsenko, *Zh. Obshch. Khim., 53,* 1983, 474; (b) E. A. Monin, Z. S. Novikova, A. A. Borisenko, M. M. Kabachnik, I. F. Lutsenko, A. N. Chernega, M. Yu. Antipin, Yu. T. Struchkov, *Zh. Obshch. Khim., 56,* 1986, 1988.
[8] N. H. Tran Huy, L. Ricard, F. Mathey, *Organometallics, 16,* 1997, 4501.
[9] A. Marinetti, F. Mathey, *Organometallics, 6,* 1987, 2189.