Nickel(II)-Promoted Homocoupling Reaction of 2-(Phosphininyl)halogenozirconocene Complexes: A New and Efficient Synthesis of 2,2′-Biphosphinines

Patrick Rosa, Nicolas Mézailles, François Mathey,* and Pascal Le Floch*

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

Received February 9, 1998

Over the past few years, we and other groups have been interested in the derivatization of phosphinines[1] in view of their use as elementary building blocks in the elaboration of sp^2-based phosphorus edifices and as ligands for homogeneous catalysis.[2] Among the most promising structures, we have shown that 2,2′-biphosphinines, the phosphorus analogues of bipyridines, reveal a significant potential in coordination chemistry for the stabilization of electron-rich and highly reduced transition-metal complexes.[3] Nevertheless, all of the complexes known to date have been synthesized with the 4,4′,5,5′-tetramethyl derivative (tmbp), which remains the most readily accessible ligand of this class. In such a context, it is clear that further progress in this area will depend on the successful synthesis of functional biphosphinines with tailored electronic properties. The coupling of P=C units is a current problem in the chemistry of low-coordinated phosphorus compounds. Indeed, despite some successful synthetic approaches derived from carbon chemistry,[4] the use of nucleophilic reagents, which tend to react at the electropositive P-atom,[5] must be avoided. From phosphinines, various synthetic approaches giving free biphosphinines[6] or their complexes[6c,7,8b] have been studied, but in most cases, their scope is limited to a specific substitution pattern of the ligand. Of the many strategies available, only four procedures are successful at generating free ligands. The first, which is limited to the preparation of tmbp, is a multistep sequence involving a cobalt(II)-promoted homocoupling reaction of [4 + 2] cycloadducts of phosphinine sulfides.[6a] Another multistep approach involving a ring expansion of 2,2′-biphospholes sulfides gives an interesting 6,6′-bis-(ethoxycarbonyl) derivative of tmbp.[6b] A catalyzed Pd(0) cross-coupling reaction between tin and polybromo derivatives has also been used to synthesize two isomers of a dibromobiphosphinine.[6c] Finally, the last method, which turns out to be the most efficient for the synthesis of both tmbp and the 3,3′-dimethyl substituted derivative, relies on the reactivity of 2-bromophosphinine−LiTMP adducts.[6d] Taking these results into consideration, we decided to reinvestigate the synthesis of biphosphinines. Among different possibilities, we focused our attention on nickel(II)-promoted homocoupling reactions of (2-phosphininyl)halogenozirconocene complexes,[9] which are, together with the zinc compounds developed by Bickelhaupt et al.,[8] the only available C-organometallic derivatives of highly electropositive metals. Our first experiments were conducted with the 4,5-dimethylphosphinine complex **1b**, which is easily obtained when reacting zirconocene (prepared using Negishi's method)[10] with 2-bromophosphinine **1a**.[9] Whereas no satisfactory results were obtained on reacting **1b** with $[NiL_2CL_2]$[11] complexes having a trans stereochemistry (L = PMe_3, PBu_3, ...) in THF at reflux, a clean coupling was observed when the *cis*-$[Ni(dppe)Cl_2]$ complex was used. After 45 min of heating in THF at reflux, the ^{31}P NMR spectrum of the reaction mixture showed the formation of the [Ni(tmbp)-(dppe)] complex **1c**, which is characterized by a classical A_2X_2 spin system located at 55.25 (dppe) and 192.30 ppm (tmbp, $\Sigma J(P-P)$ = 49.20 Hz). Complex **1c** had been previously synthesized through the reaction of tmbp and a [Ni(dppe)(olefin)] complex.[6d] Here, the formation of **1c** can be easily rationalized on the basis of a two-step process that first involves a double C−Zr to C−Ni bond metathesis,[12] leading to an intermediate Ni(II) complex, followed by a classical reductive elimination favored by the imposed cis stereochemistry (Scheme 1).

To complete this coupling sequence, we have found that hexachloroethane can be used to oxidize the [Ni(dppe)-(tmbp)] complex, giving free biphosphinine **1d** with the concomitant release of $[Ni(dppe)Cl_2]$ complex. This general approach can be extended without any difficulties to the synthesis of various biphosphinines having different substitution pattern, including the parent compound

(1) For general reviews on phosphinine chemistry, see: (a) Märkl, G. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: New York, 1990; p 220. (b) Hewitt, G. G. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: New York, 1996; Vol. 5, p 639.

(2) For the use of phosphinines in homogeneous catalysis, see: (a) Knoch, F.; Kremer, U.; Zenneck, U.; Le Floch, P.; Mathey, F. *Organometallics* **1996**, *15*, 2713. (b) Böhm, D.; Geiger, H.; Knoch, F.; Kummer, S.; Le Floch, P.; Mathey, F.; Schmidt, U.; Zenneck, U. *Phosphorus Sulfur* **1996**, *109*, 173. (c) Breit, B. *J. Chem. Soc., Chem. Commun.* **1996**, 2071. (d) Breit, B.; Winde, R.; Harms, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2681. (d) Le Floch, P.; Knoch, F.; Kremer, F.; Mathey, F.; Scholz, J.; Scholz, W.; Thiele, K.-H.; Zenneck, U. *Eur. J. Inorg. Chem.* **1998**, 119.

(3) Mathey, F.; Le Floch, P. *Chem. Ber.* **1996**, *129*, 263.

(4) (a) van der Sluis, M.; Wit, J. B. M.; Bickelhaupt, F. *Organometallics* **1996**, *15*, 174. (b) van der Sluis, M.; Beverwijk, V.; Termaten, A.; Gavrilova, E.; Bickelhaupt, F.; Kooijman, H.; Veldman, N.; Spek, A. L. *Organometallics* **1997**, *16*, 1144. (c) Cénac, N.; Chrostowska, A.; Sotiropoulos, J.-M.; Donnadieu, B.; Igau, A.; Pfister-Guillouzo, G.; Majoral, J. P. *Organometallics* **1997**, *16*, 4551.

(5) (a) Märkl, G.; Lieb, F.; Merz, A. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 87. (b) Märkl, G.; Merz, A. *Tetrahedron Lett.* **1971**, *17*, 1215. (c) Ashe, A. J., III; Smith, T. W. *Tetrahedron Lett.* **1977**, *5*, 407.

(6) (a) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1991**, *113*, 667. (b) Holand, S.; Ricard, L.; Mathey, F. *J. Org. Chem.* **1991**, *56*, 4031. (c) Trauner, H.; Le Floch, P.; Lefour, J. M.; Ricard, L.; Mathey, F. *Synthesis* **1995**, *6*, 717. (d) Le Floch, P.; Ricard, L.; Mathey, F. *Bull. Soc. Chim. Fr.* **1994**, *131*, 330.

(7) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F.; Jutand, A.; Amatore, C. *Organometallics* **1992**, *11*, 2475.

(8) (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) Teunissen, H. T.; Bickelhaupt, F. *Organometallics* **1996**, *15*, 794. (d) Teunissen, H. T.; Bickelhaupt, F. *Organometallics* **1996**, *15*, 802.

(9) Le Floch, P.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1993**, 789.

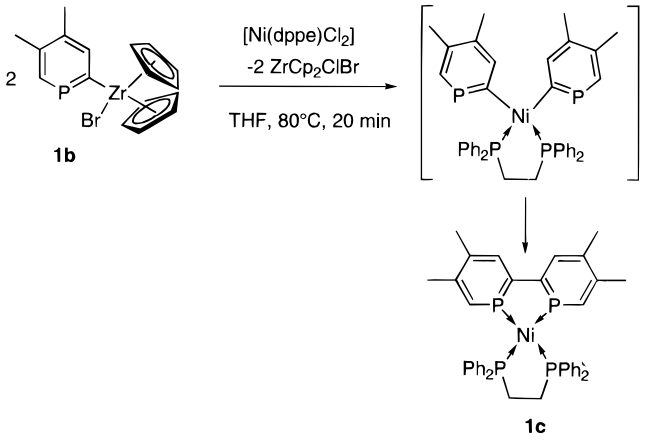
(10) Negishi, E.; Holmes, S. J.; Tour, J. H.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. S.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336.

(11) Sacconi, L.; Mani, F.; Bencini, A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 5, p 1.

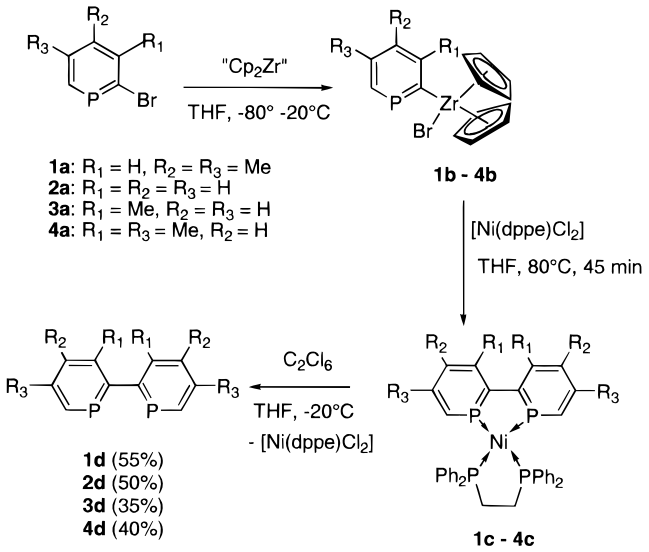
(12) (a) Negishi, E.; Van Horn, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 3168. (b) Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254.

S0022-3263(98)00230-8 CCC: $15.00
Published on Web 06/13/1998

Scheme 1



Scheme 2



$C_{10}H_8P_2$ (**2d**), which was unknown so far. Apparently, the presence of methyl groups at the C_3 position with phosphinines **3a** and **4a** does not prevent the coupling, although yields are slightly lower in these two cases. Interestingly, we also found that the coupling sequence can be carried out in the same flask from 2-bromophosphinines **1a**−**4a** since intermediate [Ni(dppe)(biphosphinine)] complexes **1c**−**4c** need not be isolated before the oxidation step (Scheme 2).

In conclusion, we have developed a new rational and efficient approach to 2,2′-biphosphinines that seems not to be dependent on the substitution scheme of the initial bromophosphinine. It opens the way toward the synthesis of polyfunctional ligands, especially 6,6′-difunctionalized 2,2′-biphosphinines. More systematic investigations on the scope of this reaction as well as on the use of 2-(phosphininyl) halogenozirconocene complexes as partners for cross-coupling reactions[12,13] will be reported in due course.

Experimental Section

Starting Materials and General Procedures. General procedures and methods for characterization have been reported previously.[5c] Phosphinines **1**−**4a** (corresponding references quoted in ref 7) and [Ni(dppe)Cl_2][14] were prepared according to published procedures.

General Procedure for the Synthesis of 2,2′-Biphosphinines. The synthesis of **1d** is typical. A solution (18.50 mL, 29.60 mmol) of *n*-butyllithium (1.6 M in hexanes) was added at −78 °C to a solution of $ZrCp_2Cl_2$ (4.32 g, 14.78 mmol) in THF (120 mL). After 20 min of stirring, a few drops of TMSCl were added to neutralize the excess of BuLi. The resulting solution was then stirred for an additional 5 min before phosphinine **1a** (3.00 g, 14.78 mmol) was added. The flask was then warmed to 30 °C for 1 h. After this period, complete formation of complex **1b**[7a] was observed by ^{31}P NMR spectroscopy. The volume of solvent was reduced to 60 mL before [Ni(dppe)Cl_2] (3.89 g, 7.39 mmol) was added. The resulting solution was heated at 80 °C, and the formation of complex **1c** was monitored by ^{31}P NMR. After 20 min, the flask was cooled to −20 °C, and hexachloroethane (1.75 g, 7.39 mmol) was added in one portion. The reaction mixture was then warmed to room temperature and stirred for an additional 30 min. The solvent was then evaporated under vacuum, and the black mixture obtained was extracted three times with dry ether. The resulting ether solution was then quickly filtrated on an alumina column. The evaporation of the solvent yielded **1d** as a yellow powder (purity up to 90%). After a rapid chromatography on silica gel using dry hexane or pentane as eluent, **1d** was recovered as yellow needles. Yield: 1.00 g (55%). For characterizations: **1b**, see ref 7, **1c**, see ref 5d, **1d**, see ref 5a.

Synthesis of 2,2′-Biphosphinine 2d. Complex **2b** was prepared from $ZrCp_2Cl_2$ (2.34 g, 8 mmol), BuLi (10 mL), and phosphinine **2a** (1.4 g, 8 mmol). Complex **2c** was prepared by reacting **2b** with [Ni(dppe)Cl_2] (2.08 g, 4 mmol). After oxidation with hexachloroethane (0.96 g, 4 mmol) and purification by chromatography on silica gel, **2d** was isolated as a colorless oil. Yield: 0.38 g (50%). **2b**: ^{31}P NMR (THF) δ 237.85. **2c**: ^{31}P NMR (THF) δ 201.85 (vt, A_2X_2, $\Sigma JP-P) = 53.10$ Hz, $C_{10}H_8P_2$), 55.45 (vt, A_2X_2, dppe). **2d**: ^{31}P NMR ($CDCl_3$) δ 196.85; ^{1}H NMR ($CDCl_3$) δ 8.81 (m, ABCDXX′, 2H, $H_{6,6'}$), 8.08 (m, ABCDXX′, 2H, $H_{3,3'}$), 7.88 (m, ABCDXX′, 2H, $H_{5,5'}$), 7.64 (m, ABCDXX′, 2H, $H_{4,4'}$); ^{13}C NMR ($CDCl_3$) δ 173.20 (m, AXX′, $|^1J(C-P_A) + {}^2J(C-P_B)| = 29.05$ Hz, $C_{2,2'}$), 155.10 (m, AXX′, $|^1J(C-P_A) + {}^4J(C-P_B)| = 51.80$ Hz, $C_{6,6'}$), 134.05 (vt, AXX′, $|\Sigma J(C-P)| = 3.30$ Hz, $C_{3,3'}$), 133.00 (vt, AXX′, $|\Sigma J(C-P)| = 12.10$ Hz, $C_{4,4'}$ or $C_{5,5'}$), 130.35 (vt, AXX′, $|\Sigma J(C-P)| = 17.25$ Hz, $C_{4,4'}$ or $C_{5,5'}$); C_2 and C_6 were simulated independently, with J(C−P) estimated initially from their values in **1d**. Subsequent iteration (giving $^1J(C-P) = -57.50$ Hz, $^4J(C-P) = 5.75$ Hz for C_6, and $^1J(C-P) = -55.00$ Hz, $^3J(C-P) = 25.95$ Hz for C_2) converged upon $^3J(P-P)$ of 63.50 with a ^{13}C isotopic shift upon adjacent ^{31}P nucleus of 8.5×10^{-2}; MS *m/z* 190 (M, 100). Anal. Calcd for $C_{10}H_8P_2$: C, 63.18; H, 4.24. Found: C, 63.50; H, 4.28.

Synthesis of 3,3′-Dimethyl-2,2′-biphosphinine 3d. Complex **3b** was prepared from $ZrCp_2Cl_2$ (1.55 g, 5.30 mmol), BuLi (6.70 mL), and bromophosphinine **3a** (1.0 g, 5.30 mol). Complex **3c** was prepared by reacting **3b** with [Ni(dppe)Cl_2] (1.40 g, 2.65 mmol). After oxidation with hexachloroethane (0.63 g, 2.65 mmol) and purification by chromatography on silica gel using hexane as eluent, **3d** was isolated as a colorless oil. Yield: 0.20 g (35%). For characterization of **3b**, see ref 7. **3c**: ^{31}P NMR (THF) δ 201.95 (vt, A_2X_2, $\Sigma J(P-P) = 48.80$ Hz, $C_{12}H_{12}P_2$), 52.27 (vt, A_2X_2, dppe). **3d**: see ref 5e.

Synthesis of 2-Bromo-3,5-dimethylphosphinine (4a). The reaction was carried out in a 2 L flask. A solution of Br_2-PCHBr_2 (36.40 g, 0.10 mol) in THF (50 mL) was added dropwise to a mixture of 2-methyl-1,3-pentadiene (82.00 g, 1 mol), triethylamine (25.25 g, 0.25 mol), and THF (200 mL) at 60 °C (2 h). At the end of the addition, the reaction mixture was stirred for an additional 30 min at 60 °C. Then, the excess of diene and the half part of the solvent were evaporated. Triethylamine (50.00 g, 0.50 mol) and THF (100 mL) were added, and the resulting mixture was heated at 80 °C. The formation of phosphinine **4a** was monitored by ^{31}P NMR spectroscopy. After 2 h, the flask was cooled to room temperature, and dry hexane (200 mL) was added to precipitate the most part of the Et_3N·HBr salt. The solution was then filtrated. After evaporation of the

(13) (a) Schwartz, J.; Loots, M. J.; Kosugi, H. *J. Am. Chem. Soc.* **1980**, *102*, 1333. (b) Dayrit, F. M.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 4466.

(14) Booth, J.; Chatt, J. *J. Chem. Soc.* **1965**, 3238.

solvent, the brown oil obtained was partially dissolved in hexane (50 mL) and chromatographed on silica gel with hexane as eluent. After evaporation of hexane, **4a** was recovered as a slightly oxygen-sensitive colorless oil: yield 12.20 g (60%); ^{31}P NMR ($CDCl_3$) δ 206.95; ^{1}H NMR ($CDCl_3$) δ 8.12 (ddq, ^2J(H−P) = 41.30 Hz, ^4J(H−H_4) = 1.40 Hz, ^4J(H−Me) = 0.55 Hz, 1H, H_6), 7.24 (ddq, ^4J(H−H_6) = 1.40 Hz, ^4J(H−Me) = 0.60 Hz, ^4J(H−P) = 5.05 Hz, 1H, H_4), 2.59 (d, ^4J(H−P) = 2.30 Hz, 3H, *Me*-C_3), 2.46 (dd, ^4J(H−H_4) = 0.60 Hz, ^4J(H−H_6) = 0.55 Hz, 3H, *Me*-C_5); ^{13}C NMR ($CDCl_3$) δ 155.30 (d, ^1J(C−P) = 52.80 Hz, C_6), 150.60 (d, ^1J(C−P) = 64.05 Hz, C_2), 144.90 (d, J(C−P) = 15.25 Hz, C_3 or C_5), 143.40 (d, J(C−P) = 14.10 Hz, C_5 or C_3), 135.45 (d, ^3J(C−P) = 15.80 Hz, C_4), 26.40 (s, Me), 24.90 (d, J(C−P) = 3.65 Hz, Me); MS *m*/*z* 202 (M, 70), 121 (M − HBr, 80). Anal. Calcd for C_7H_8BrP: C, 41.41; H, 3.97. Found: C, 41.78; H, 4.05.

Synthesis of 3,3′5,5′-Tetramethyl-2,2′-biphosphinine (4d). Complex **4b** was prepared from $ZrCp_2Cl_2$ (2.92 g, 10 mmol), BuLi (12.50 mL), and bromophosphinine **4a** (2.00 g, 10 mmol). Complex **4c** was prepared by reacting **4b** with Ni(dppe)Cl_2 (2.64 g, 2.65 mmol). After oxidation with hexachloroethane (1.20 g, 2.65 mmol) and purification by chromatography on silica gel with pentane as eluent, **4d** was isolated as a colorless oil. Yield: 0.49 g (40%). **4b**: ^{31}P NMR (THF) δ 219.45 (^2J(H−P) = 45.30 Hz). **4c**: ^{31}P NMR (THF) δ 202.35 (vt, A_2X_2, ΣJ(P−P) = 49.75 Hz, $C_{14}H_{16}P_2$), 53.30 (vt, A_2X_2, dppe). **4d**: ^{31}P NMR ($CDCl_3$) δ 200.65; ^{1}H NMR ($CDCl_3$) δ 8.38 (m, AA′XX′, 2H, $|\Sigma J$(H−P)| = 39.07 Hz, $H_{6,6'}$), 7.23 (bs, 2H, $H_{4,4'}$), 2.50 (s, 6H, Me), 2.13 (s, 6H, Me); ^{13}C NMR ($CDCl_3$) δ 168.30 (AXX′, $|\Sigma J$(C−P)| = 22.90 Hz, $C_{2,2'}$), 152.55 (AXX′, $|\Sigma J$(C−P)| = 53.60 Hz, $C_{6,6'}$), 143.85 (AXX′, $|\Sigma J$(C−P)| = 12.25 Hz, $C_{5,5'}$ or $C_{3,3'}$), 142.35 (s, $C_{3,3'}$ or $C_{5,5'}$), 134.55 (AXX′, $|\Sigma J$(C−P)| = 15.10 Hz, $C_{4,4'}$), 25.25 (s, Me), 23.30 (s, Me); MS *m*/*z* 246 (M, 100), 231 (M − Me, 40). **4d** turned out to be too oxygen sensitive to give a satisfactory elemental analysis.

Acknowledgment. The authors thank the CNRS and the Ecole Polytechnique for supporting this work.

JO980230K