

2.407 (28) Å for Si-Si distances in a cyclotrisilane, Si<sub>3</sub>R<sub>6</sub> (where R = 2,6-dimethylphenyl).<sup>25</sup> Using the values for Si<sub>3</sub> and Ge<sub>3</sub> clusters, Si and Ge "cluster covalent radii" of 1.2035 and 1.2705 Å may be calculated, leading to a predicted Si-Ge cluster bond distance of 2.474 Å. On the assumption that the disorder is 3-fold and that the Ge-Ge distance (from 2) is 2.538 Å, we can calculate a Si-Ge distance of 2.493 Å from the expression  $\frac{1}{3}[d(\text{Ge-Ge}) + 2d(\text{Si-Ge})] = 2.508 \text{ \AA}$ . This value differs little from that predicted above of 2.474 Å but is also much longer than the mean Si-Ge distances reported for Ph<sub>3</sub>Si-GeMe<sub>3</sub> (2.394 (1) Å),<sup>11</sup> Me<sub>3</sub>Si-GePh<sub>3</sub> (2.384 (1) Å),<sup>12</sup> and a germatrisilacyclobutane (2.457 (7) Å).<sup>10</sup> It is interesting to note that the Ge-Ge distances observed in cyclotragermanes (ref 22 and this work) are also longer than those found for linear

and less strained molecules. This elongation of bond lengths is probably to be expected for three-membered rings with bulky substituents, due to steric congestion.<sup>22,25</sup> The M-C distances within compound 1 are 2.013, 2.010, and 2.011 Å, mean 2.011 (2) Å. Other distances and angles within both compounds are normal.

**Acknowledgment.** We thank the NSERC of Canada and the University of Western Ontario for financial support of this work in the form of grants to K.M.B. and N.C.P.

**Registry No.** 1, 138432-97-0; 2, 138432-98-1.

**Supplementary Material Available:** For 1 and 2, listings of anisotropic thermal parameters, calculated hydrogen atom parameters, root-mean-square amplitudes of anisotropic displacement, and weighted least-squares planes and dihedral angles (6 pages); listings of structure amplitudes (25 pages). Ordering information is given on any current masthead page.

(25) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, M. *J. Am. Chem. Soc.* 1982, 104, 1150.

## (2-Phosphino)phospholyls: A New Type of $\eta^1, \eta^5$ -Heterodifunctional Ligand for Transition-Metal Chemistry

Bernard Deschamps and François Mathey\*

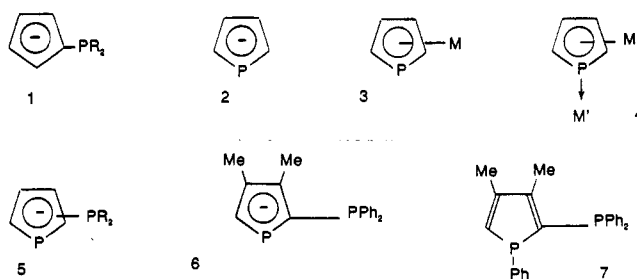
Laboratoire de Chimie du Phosphore et des Métaux de Transition, CNRS UM 13,  
DCPH Ecole Polytechnique, 91128 Palaiseau Cedex, France

Received October 21, 1991

**Summary:** The anion obtained by metalation of 1-phenyl-3,4-dimethylphosphole sulfide reacts with chlorodiphenylphosphine to give the corresponding 2-(diphenylphosphino)phosphole sulfide. A migration of sulfur slowly takes place between the two phosphorus atoms of this compound. The resulting trivalent phosphole reacts with lithium in THF to yield the 3,4-dimethyl-2-(diphenylphosphino)phospholyl anion. This anion is converted into the corresponding 2,2'-bis(diphenylphosphino)-1,1'-diphosphaferrocene by reaction with iron(II) chloride. The difunctional diphosphaferrocene thus obtained gives a Mo(CO)<sub>4</sub> chelate by reaction with molybdenum hexacarbonyl.

Phosphino-substituted cyclopentadienyls (1) have recently found a widespread use in coordination chemistry.<sup>1</sup> Their interest stems from the fact that they allow two

types of transition metals to be held in close proximity in



order to study their cooperativity in various reactions. On the other hand, phospholyls (phosphacyclopentadienyls) (2) have been shown to be able to replace cyclopentadienyls in a variety of  $\eta^5$ -complexes<sup>2</sup> (3) and to have the additional ability to coordinate a second metal via their phosphorus lone pair<sup>2</sup> (4). The previously unknown phosphino-substituted phospholyls (5) were thus a target of obvious interest for coordination chemists. We describe here the synthesis of the first such ligand, i.e. the 3,4-dimethyl-(2-diphenylphosphino)phospholyl anion (6) and some of its transition-metal complexes.

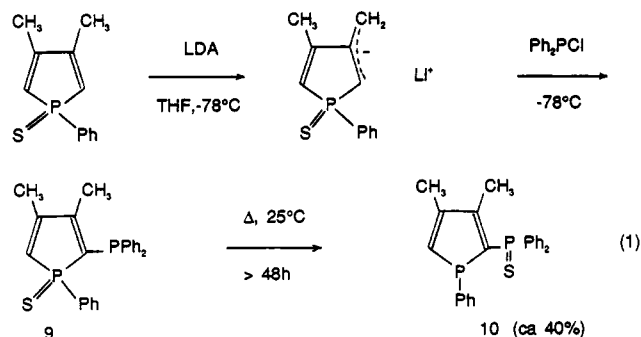
### Results and Discussion

The classical synthesis of phospholyl anions involves the cleavage of the exocyclic P-Ph bond of 1-phenylphospholes

(1) (a) Selected references: Mathey, F.; Lampin, J. P. *J. Organomet. Chem.* 1977, 128, 297. Rudig, A. W.; Lichtenberg, D. W.; Katcher, M. L.; Davison, A. *Inorg. Chem.* 1978, 17, 2859. Casey, C. P.; Bullock, R. M.; Fultz, W. C.; Rheingold, A. L. *Organometallics* 1982, 1, 1591. Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* 1983, 105, 7574. Casey, C. P.; Nief, F. *Organometallics* 1985, 4, 1218. Rausch, M. D.; Edwards, B. H.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* 1983, 105, 3882. Moise, C.; Maisonnat, A.; Poilblanc, R.; Charrier, C.; Mathey, F. *J. Organomet. Chem.* 1984, 231, C43. Tikkanen, W.; Fujita, Y.; Petersen, J. L. *Organometallics* 1986, 5, 888. Du Bois, D. L.; Eigenbrot, C. W., Jr.; Miedaner, A.; Smart, J. C.; Haltiwanger, R. C. *Organometallics* 1986, 5, 1405. He, X. D.; Maisonnat, A.; Dahan, F.; Poilblanc, R. *Organometallics* 1987, 6, 678. Anderson, G. K.; Lin, M. *Inorg. Chim. Acta* 1988, 142, 7. He, X. D.; Maisonnat, A.; Dahan, F.; Poilblanc, R. *Organometallics* 1989, 8, 2618. Rausch, M. D.; Spink, W. C.; Atwood, J. L.; Baakar, A. J.; Bott, S. G. *Organometallics* 1989, 8, 2627. Deacon, G. B.; Dietrich, A.; Forsyth, C. M.; Schumann, H. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1370. He, X. D.; Maisonnat, A.; Dahan, F.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* 1990, 670. Szymoniak, J.; Kubicki, M. M.; Besançon, J.; Moise, C. *Inorg. Chim. Acta* 1991, 180, 153. Schenk, W. A.; Neuland-Labude, C. *Z. Naturforsch* 1991, 46B, 573. Anderson, G. K.; Lin, M.; Chiang, M. Y. *Organometallics* 1990, 9, 288. Anderson, G. K.; Lin, M.; Rath, N. P. *Organometallics* 1990, 9, 2880. Tikkanen, W.; Ziller, J. W. *Organometallics* 1991, 10, 2266. He, X. D.; Maisonnat, A.; Dahan, F.; Poilblanc, R. *Organometallics* 1991, 10, 2443. Wong, W.-K.; Chow, F. L.; Chen, H.; Wang, R.-J.; Mak, T. C. W. *Polyhedron* 1990, 9, 2469.

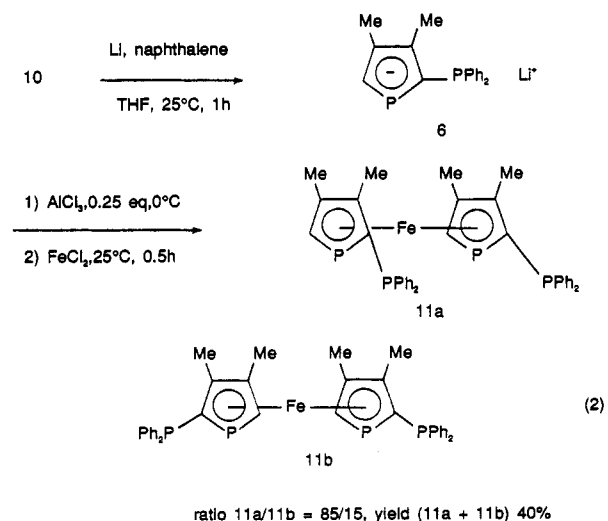
(2) Review: Mathey, F. *New J. Chem.* 1987, 11, 585. Recent references: Nief, F.; Mathey, F.; Ricard, L.; Robert, F. *Organometallics* 1988, 7, 921. Nief, F.; Mathey, F. *J. Chem. Soc., Chem. Commun.* 1988, 770. Nief, F.; Ricard, L.; Mathey, F. *Organometallics* 1989, 8, 1473. Nief, F.; Mathey, F. *J. Chem. Soc., Chem. Commun.* 1989, 800. Nief, F.; Mathey, F.; Ricard, L. *J. Organomet. Chem.* 1990, 384, 271. Baudry, D.; Ephritikhine, M.; Nief, F.; Ricard, L.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* 1990, 29, 1485. Nief, F.; Mathey, F. *Synlett* 1991, 745. Kershner, D. L.; Basolo, F. *J. Am. Chem. Soc.* 1987, 109, 7396. Roberts, R. M. G.; Silver, J.; Wells, A. S. *Inorg. Chim. Acta* 1989, 155, 197. Roberts, R. M. G.; Silver, J.; Wells, A. S. *Inorg. Chim. Acta* 1989, 157, 45. Lemoine, P. *J. Organomet. Chem.* 1989, 359, 61. Metternich, H. J.; Niecke, E. *Angew. Chem., Int. Ed. Engl.* 1991, 30, 312. Chase, K. J.; Bryan, R. F.; Woode, M. K.; Grimes, R. N. *Organometallics* 1991, 10, 2631.

by alkali metals.<sup>3</sup> The normal precursor of **6** is thus 1-phenyl-3,4-dimethyl-2-(diphenylphosphino)phosphole (**7**). Previous attempts to prepare **7** from the appropriate phospholene rings have failed.<sup>4</sup> We were thus led to a different approach relying on the metalation of 1-phenyl-3,4-dimethylphosphole sulfide (**8**).<sup>5</sup> A careful optimization of the metalation procedure was first carried out. As a result, we selected lithium diisopropylamide (LDA) as the best metalating agent in lieu of the previously used *tert*-butyllithium. The functionalization was straightforward (eq 1). The resulting 2-(diphenyl-



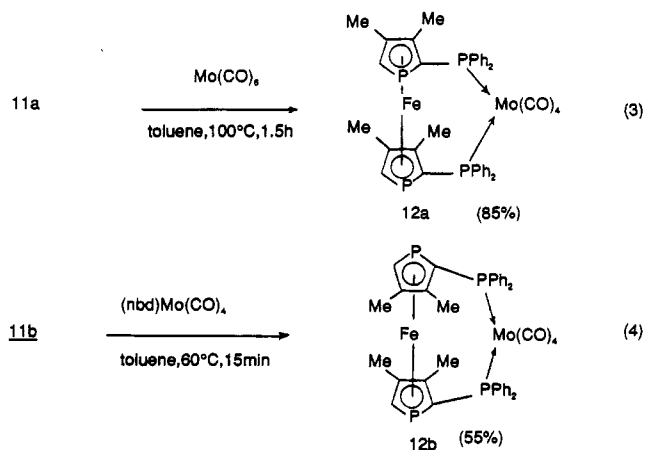
phosphino)phosphole sulfide (**9**) was characterized by <sup>31</sup>P NMR spectroscopy (CH<sub>2</sub>Cl<sub>2</sub>): δ(PPh<sub>2</sub>) -17 ppm, δ(P(S)Ph) +53 ppm, <sup>2</sup>J(P-P) ca. 0 Hz. Upon standing at room temperature, **9** slowly transforms into **10**. This internal reduction is not surprising since phosphole sulfides are known to be easily reduced by ordinary tertiary phosphines.<sup>5</sup> The <sup>31</sup>P NMR data for **10** are strikingly different from those for **9**: δ(P(S)Ph<sub>2</sub>) +30.5 ppm, δ(PPh) +12.5 ppm, <sup>2</sup>J(P-P) = 56 Hz. The drastic increase in the <sup>2</sup>J(P-P) coupling constant when going from **9** to **10** probably results from the blocking of the PPh<sub>2</sub> group in a different conformation before and after sulfurization.

The stable compound **10** proved to be a convenient precursor for the anion **6**. Lithium wire (containing ca. 1% sodium) in the presence of naphthalene in THF is able both to reduce the P=S bond and to cleave the phosphole P-Ph bond (eq 2). The resulting phospholyl anion (**6**) is



characterized by <sup>31</sup>P NMR spectroscopy: AX system δ<sub>A</sub>-

(phospholyl) +89 ppm, δ<sub>X</sub>(PPh<sub>2</sub>) -17 ppm, <sup>2</sup>J(P-P) = 122 Hz. The enormous increase of the <sup>2</sup>J(P-P) coupling when going from **10** to **6** is probably indicative of the partial double-bond character of the phospholyl P-C bonds.<sup>6</sup> An additional demonstration of the formation of **6** was provided by its reaction with FeCl<sub>2</sub> in the presence of AlCl<sub>3</sub>,<sup>7a</sup> which gives the corresponding 1,1'-diphosphaferrocene **11** (eq 2). The two isomeric diphosphaferrocenes **11a** and **11b** were fully characterized by NMR and mass spectroscopies. They show a characteristic shift to high field of the phospholyl <sup>31</sup>P resonance<sup>7b</sup> (CH<sub>2</sub>Cl<sub>2</sub>): **11a** δ(PPh<sub>2</sub>) -18.9 ppm, δ(cyclic P) -56.7 ppm, <sup>2</sup>J(P-P) = 12.2 Hz; **11b** δ(PPh<sub>2</sub>) -18.4 ppm, δ(cyclic P) -63.7 ppm, <sup>2</sup>J(P-P) ~ 0 Hz. In both isomers, the diphenylphosphino groups retain a high ability to coordinate additional transition metals. This was shown as the reaction with molybdenum carbonyl as a model (eqs 3 and 4). A preliminary X-ray



crystal structure analysis of **12a**<sup>8</sup> showed that it contains a plane of symmetry, thus establishing the stereochemistry of **11a** and **11b**.

### Experimental Section

NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for <sup>1</sup>H and 50.32 MHz for <sup>13</sup>C and on a Bruker WP 80 SY spectrometer operating at 32.43 MHz for <sup>31</sup>P. Chemical shifts are expressed in parts per million downfield from internal TMS (<sup>1</sup>H and <sup>13</sup>C) and external 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Coupling constants are expressed in hertz. Mass spectra were obtained at 70 eV with a Shimadzu GC-MS QP 1000 instrument by the direct-inlet method. Infrared spectra were recorded on a Perkin-Elmer Model 297 spectrometer. Elemental analyses were performed by the "Service d'analyse du CNRS", Gif-sur-Yvette, France. Silica gel (70-230 mesh) was used for chromatographic separations. All commercially available reagents were used as received from the suppliers.

**1-Phenyl-(2-diphenylthiophosphoryl)-3,4-dimethylphosphole (10).** To a stirred solution of 1-phenyl-3,4-dimethylphosphole sulfide<sup>9</sup> (2.2 g, 1 × 10<sup>-2</sup> mol) and *N,N,N',N'*-tetramethylethylenediamine (2.25 mL, 1.5 × 10<sup>-2</sup> mol) in THF (30 mL) was added at -80 °C 1.2 × 10<sup>-2</sup> mol of lithium diisopropylamide [prepared from diisopropylamine (1.7 mL, 1.2 × 10<sup>-2</sup> mol) and *n*-butyllithium (7.5 mL, 1.6 N) in THF (20 mL)]. The solution became red. After 10 min, chlorodiphenylphosphine (3.6 mL, 2 × 10<sup>-2</sup> mol) was added to this solution, which became colorless. After a further 10 min, 20 mL of 3 N HCl was added

(6) Karsch, H. H.; Köhler, F. H.; Reischer, H. U. *Tetrahedron Lett.* 1984, 25, 3687.

(7) (a) AlCl<sub>3</sub> serves to destroy PhLi which is formed as a byproduct in the synthesis of the phospholyl anions and to catalyze the formation of the P-Fe bonds, see: Mathey, F.; de Lauzon, G. *Organomet. Synth.* 1986, 3, 256. (b) de Lauzon, G.; Deschamps, B.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* 1980, 102, 994.

(8) Ricard, L. Unpublished results.

(9) Brèque, A.; Mathey, F.; Savignac, P. *Synthesis* 1981, 983.

(3) Braye, E. H.; Caplier, I.; Saussez, R. *Tetrahedron* 1971, 27, 5523. For a review on phospholes and phospholyl anions, see: Mathey, F. *Chem. Rev.* 1988, 88, 429.

(4) Amin, M.; Holah, D. G.; Hughes, A. N.; Rukachaisirikul, T. *J. Heterocycl. Chem.* 1985, 22, 513.

(5) Mathey, F. *Tetrahedron Lett.* 1973, 3255. Mathey, F. *Tetrahedron* 1974, 30, 3127; 1976, 32, 2395.

and the mixture was allowed to warm to room temperature. THF was evaporated, and the residue was extracted with  $\text{CH}_2\text{Cl}_2$ , washed with distilled water, and dried over  $\text{MgSO}_4$ . A filtration through silica gel was performed to eliminate heavy compounds; dichloromethane was evaporated, and the residue was allowed to stand under argon for at least 48 h. During this time, **9** was transformed into **10**. The mixture was chromatographed with toluene. Yield of **10**: 1.6 g (40%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.14 (s, 3 H, Me), 2.27 (m, 3 H, Me), 6.6-7.8 (m, 16 H, Ph + HC-P).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  17.69 (s, Me), 17.82 (s, Me), 149.97 (dd,  $^2J(\text{C-P}) = 6.6$  Hz,  $^3J(\text{C-P}) = 16.5$  Hz,  $\text{C}_\beta$ ), 161.31 (dd,  $^2J(\text{C-P}) = 12.6$  and  $5.5$  Hz,  $\text{C}_\alpha$ ). Mass spectrum:  $m/z$  404 ( $\text{M}^+$ , 87%), 217 ( $\text{Ph}_2\text{PS}$ , 100%). Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{P}_2\text{S}$ : C, 71.27; H, 5.48. Found: C, 70.84; H, 5.20.

**3,3',4,4'-Tetramethyl-2,2'-bis(diphenylphosphino)-1,1'-diphosphaferrocenes (11a and 11b).** To a stirred solution of **10** (1 g,  $2.5 \times 10^{-3}$  mol) in THF (20 mL) were added lithium wire (0.05 g,  $7.2 \times 10^{-3}$  mol) and naphthalene (0.5 g,  $5 \times 10^{-3}$  mol) at room temperature. After 1 h, the mixture was cooled at  $0^\circ\text{C}$  and aluminum chloride (0.08 g,  $6 \times 10^{-4}$  mol) was added. After 30 min, the mixture was allowed to warm to room temperature and iron(II) chloride (0.16 g,  $1.25 \times 10^{-3}$  mol) added. After an additional 30 min, the THF was evaporated and the residue chromatographed with hexane/toluene 50/50 as the eluent. Two isomers **11a** and **11b** were obtained in an 85/15 ratio. Total yield (**11a** + **11b**):  $\sim 0.3$  g (40%).

**11a:**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.00 (s, 6 H, Me), 2.13 (s, 6 H, Me), 3.90 (d,  $^2J(\text{H-P}) = 35.6$  Hz, 2 H, CH-P);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  14.50 (d,  $^3J(\text{C-P}) = 15$  Hz, Me), 16.31 (s, Me), 85.42 (d,  $^1J(\text{C-P}) = 63.2$  Hz,  $\text{C}_5\text{H}$ ), 93.85 (dd,  $^1J(\text{C-P}) = 80.6$  and  $15.8$  Hz,  $\text{C}_2\text{P}$ ), 100.20 (dd,  $^2J(\text{C-P}) = 20.8$  and  $5.6$  Hz,  $\text{C}_3$ ), 101.97 (s,  $\text{C}_4$ ); mass spectrum  $m/z$  646 ( $\text{M}^+$ , 100%), 461 ( $\text{M}^+ - \text{PPh}_2$ , 57%). Anal. Calcd for  $\text{C}_{36}\text{H}_{34}\text{P}_4\text{Fe}$ : C, 66.89; H, 5.30. Found: C, 66.22; H, 5.27.

**11b:**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.95 (s, 6 H, Me), 2.21 (s, 6 H, Me), 3.74 (m, 2 H, CH-P);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  12.65 (d,  $^3J(\text{C-P}) = 15.5$  Hz, Me), 14.28 (s, Me), 83.32 (m,  $\text{C}_5\text{H}$ ), 100.92 (m,  $\text{C}_3$ ), 103.16 (s,  $\text{C}_4$ ). The loss of symmetry in **11b** (vs **11a**) explains the appearance of higher-order patterns in the  $^1\text{H}$  and  $^{13}\text{C}$  spectra, thus confirming the structural assignments made on the basis of the preliminary X-ray study of **12a**.

**[3,3',4,4'-Tetramethyl-2,2'-bis(diphenylphosphino)-1,1'-diphosphaferrocene]tetracarbonylmolybdenum (12a and 12b).** Two different experiments were performed: (1) Diphosphaferrocene **11a** (0.28 g,  $0.43 \times 10^{-3}$  mol) was heated at  $100^\circ\text{C}$  in 5 mL of toluene with molybdenum hexacarbonyl (0.12 g,  $0.46 \times 10^{-3}$  mol) for 90 min. Toluene was removed, and the residue was chromatographed with hexane/toluene 50/50 as the eluent. Yield of **12a**: 0.32 g (85%). (2) Diphosphaferrocene **11b** (0.11 g,  $0.17 \times 10^{-3}$  mol) was heated at  $60^\circ\text{C}$  in 5 mL of toluene with norbornadiene-Mo(CO)<sub>4</sub> (0.05 g,  $0.17 \times 10^{-3}$  mol) for 15 min. Toluene was removed and the residue chromatographed as before. Yield of **12b**: 0.08 g (55%).

**12a:**  $^{31}\text{P NMR}$  ( $\text{CH}_2\text{Cl}_2$ )  $\delta(\text{PPh}_2) +34.7$ ,  $\delta(\text{cyclic P}) -54$  (both resonances appear as complex multiplets);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.60 (s, 6 H, Me), 1.88 (s, 6 H, Me), 3.70 (m, 2 H, CH-P);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  13.99 (s, Me), 14.66 (s, Me), 80.22 (m,  $\text{C}_5\text{H}$ ), 99.72 (m,  $\text{C}_3$ ), 102.88 (m,  $\text{C}_4$ ). Anal. Calcd for  $\text{C}_{40}\text{H}_{34}\text{O}_4\text{P}_4\text{FeMo}$ : C, 56.21; H, 3.98. Found: C, 56.59; H, 3.93.

**12b:**  $^{31}\text{P NMR}$  (toluene)  $\delta(\text{PPh}_2) +35.6$ ,  $\delta(\text{cyclic P}) -42.7$  (both resonances appear as complex multiplets);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.25 (s, 6 H, Me), 2.31 (s, 6 H, Me), 3.62 (m, 2 H, CH-P).

**Registry No.** **6**, 138784-72-2; **9**, 138784-68-6; **10**, 138784-69-7; **11a**, 138874-90-5; **11b**, 138784-70-0; **12a**, 138875-98-6; **12b**, 138784-71-1; 1-phenyl-3,4-dimethylphosphole sulfide, 30540-37-5; chlorodiphenylphosphine, 1079-66-9.

## Metallacarboranes as Labile Anions for Ionic Zirconocene Olefin Polymerization Catalysts

Gregory G. Hlatky,\* Richard R. Eckman,\* and Howard W. Turner\*

Exxon Chemical Company, Baytown Polymers Center, P.O. Box 5200, Baytown, Texas 77522

Received September 27, 1991

**Summary:** Anions of the type  $[(\text{C}_2\text{B}_9\text{H}_{11})_2\text{M}]^-$  ( $\text{M} = \text{Fe}$ ,  $\text{Co}$ ,  $\text{Ni}$ ) are suitable for use as "noncoordinating" anions with  $[\text{Cp}_2\text{ZrMe}]^+$  cations. Catalysts generated from  $\text{Cp}_2\text{ZrMe}_2$  and  $[\text{PhNMe}_2\text{H}][(\text{C}_2\text{B}_9\text{H}_{11})_2\text{M}]$  are active for the polymerization and copolymerization of ethylene and  $\alpha$ -olefins. Spectroscopic examination of the cobalt complex indicates that the anion is weakly coordinated to the metal at room temperature. At low temperatures, however, the aniline-coordinated adduct  $[\text{Cp}_2\text{ZrMe}(\text{NMe}_2\text{Ph})][(\text{C}_2\text{B}_9\text{H}_{11})_2\text{M}]$  is present. These catalysts are active in toluene or hexane for the polymerization of ethylene and the copolymerization of ethylene and 1-butene.

Homogeneous Ziegler-Natta polymerization catalysts based on bis(cyclopentadienyl)metal complexes of the type  $\text{Cp}'_2\text{MX}_2$ , discovered in the early 1950s,<sup>1</sup> have long been used as model systems for mechanistic studies. Whether the active catalytic species is cocatalyzed by trialkylaluminum reagents or by methylaluminoxane,<sup>2</sup> the nature of this species has for many years been the subject of

controversy. It is now generally established through many approaches, including electrochemical,<sup>3</sup> theoretical,<sup>4</sup> trapping,<sup>5</sup> XPS,<sup>6</sup> surface studies<sup>7</sup> and research on neutral isoelectronic compounds,<sup>8</sup> that the active complex is the formally three-coordinate cation  $[\text{Cp}'_2\text{MR}]^+$ .<sup>9</sup> A clear determination of the structures of these catalysts, however, has been precluded by the instability of the catalyst<sup>1a</sup> or the indeterminate nature of methylaluminoxane.

(3) (a) Zefirova, A. K.; Shilov, A. E. *Dokl. Akad. Nauk SSR* 1961, 136, 599. (b) Dyachkovskii, F. S. *Vysokomol. Soedin.* 1965, 7, 114. (c) Dyachkovskii, F. S.; Shilova, A. K.; Shilov, A. E. *J. Polym. Sci., Part C* 1967, 16, 2333.

(4) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* 1976, 98, 1729. (5) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* 1985, 107, 7219.

(6) Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* 1987, 109, 7875.

(7) Dahmen, K. H.; Hedden, D.; Burwell, R. L., Jr.; Marks, T. J. *Langmuir* 1988, 4, 1212.

(8) (a) Ballard, D. G. H.; Curtis, A.; Holton, J.; McMeeking, J.; Pearce, R. *J. Chem. Soc., Chem. Commun.* 1979, 994. (b) Watson, P. L. *J. Am. Chem. Soc.* 1982, 104, 337. (c) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* 1984, 56, 1. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* 1985, 107, 8091. (e) Den Haan, K. H.; Wielstra, Y.; Eshuis, J. J. W.; Teuben, J. H. *J. Organomet. Chem.* 1987, 323, 181.

(9) Gianetti, E.; Nicoletti, G. M.; Mazzocchi, R. *J. Polym. Sci., Polym. Chem. Ed.* 1985, 23, 2117.

(1) (a) Natta, G.; Pino, P.; Mazzanti, G.; Giannini, U. *J. Am. Chem. Soc.* 1957, 79, 2976. (b) Breslow, D. S.; Newburg, N. R. *J. Am. Chem. Soc.* 1957, 79, 5072.

(2) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* 1980, 18, 99.