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Recovering phospholes from phosphacymantrenes

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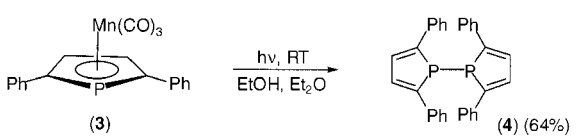
Abstract

Several attempts to recover phospholes from phosphacymantrenes are described. UV irradiation gives 1,1′-biphospholes when the ring carries two phenyl substituents. Lithium reduction appears to give somewhat erratic results. *Exo*-attack by phenyllithium leads to η^4-anionic complexes derived from the corresponding 1-phenylphospholes. Quite surprisingly, this attack by phenyllithium is compatible with a carbonyl fonctionality on the ring. These anionic complexes yield η^4-phospholium derivatives upon quaternization of phosphorus with $BrCH_2CH_2Z$ (Z = CN, COOEt). One of these phospholium complexes has been caracterized by X-ray crystal structure analysis.

Keywords: Manganese; Phospholes; Phospholium salts; Phosphacymantrenes; Nucleophilic attacks

1. Introduction

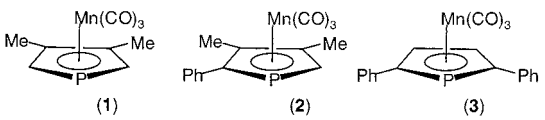
From a synthetic standpoint, the most useful characteristic of phosphacymantrenes and phosphaferrocenes is their ability to undergo electrophilic substitution reactions [1–3]. This has allowed the synthesis of several planar chiral 2-functional phosphaferrocenes which have been used in asymmetric catalysis [4–7]. From a theoretical standpoint, such chemistry is possible because of the very low energy of the sp^2-lone pair at phosphorus in both types of complexes [8,9]. By way of contrast, the pyramidal phospholes sp^3-lone pair is the HOMO of the system. Hence, electrophilic substitution reactions on phospholes are only possible when very bulky P-substituents are present to force planarisation, thus favoring the delocalisation of the lone pair over the phosphole ring [10]. At the moment, the most efficient technique for synthesizing functional phospholes relies on the bromine to lithium exchange in 2-bromophospholes [11,12]. Alternatively, it is possible to obtain some 2-functional phospholide ions using a [1,5]-sigmatropic shift of the functional group from phosphorus to the α-carbon of the ring [13,14]. Against this background, it is obviously useful to be able to convert a 2-functional phosphacymantrene or ferrocene into the corresponding phospholes. This work describes our attempts with phosphacymantrenes. The case of phosphaferrocenes appears to be more difficult to solve.



Scheme 1.

2. Results and discussion

Our first experiments were based upon an observation of Jaouen et al. [15] concerning the decomplexation of cymantrenes into cyclopentadienes by photolysis in methanol. A transposition of this technique was attempted with phosphacymantrenes (**1**–**3**).



The results were clearcut. The decomplexation was successful for the phenyl-substituted derivative (**3**) (Scheme 1) but led to a variety of decomposition products in the case of **1**.

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The resulting 1,1′-biphosphole (**4**) was characterized by ^{1}H-NMR, ^{31}P-NMR and mass spectrometry in comparison with an authentic sample. The LUMO of phosphacymantrenes is essentially an antibonding combination of the p_z(P) and d_{xz}(Mn) orbitals [16]. The promotion of an electron from the HOMO to the LUMO very probably induces a cleavage of the P–Mn bond. Product biradical then dimerizes and ultimately gives the 1,1′-biphosphole. Unfortunately, whatever its actual mechanism, this method proved to be uneffective for functional compounds such as the 2-acetyl derivative of **1**.

In a second series of experiments, we studied the reduction of phosphacymantrenes (**1**) and (**3**) by naphthalene–lithium in THF. The results observed with **3** are depicted in Scheme 2.

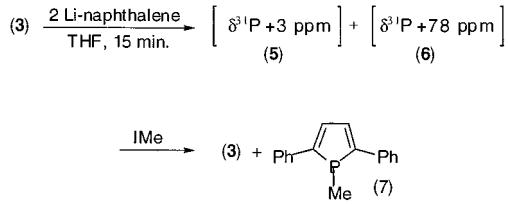
Longer reaction times did not affect the **5**/**6** ratio. The final products **3** and **7** were identified by ^{1}H-NMR, ^{31}P NMR and mass spectrometry, and by comparison with an authentic sample for **7**. Both its ^{31}P chemical shift [17] and the nature of its alkylation product demonstrate that **6** is the 2,5-diphenylphospholide ion. Since compound **5** is reoxidized into the starting product, we suspect that the actual reduction of **3** proceeds as follows (Scheme 3).

At the moment, we have been unable to get stable derivatives of **5** and the proposed mechanism remains speculative. Similar results have been obtained during the reduction of **1**. Unfortunately, we have been unable to transform completely the starting phosphacymantrenes into the corresponding phospholides and the method is obviously not compatible with reactive functional groups.

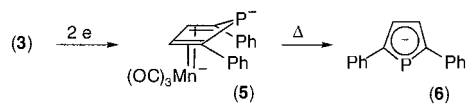
We then decided to reinvestigate the reaction of phosphacymantrenes with organolithium compounds. A preliminary study [1] showed that the treatment of **1** with butyllithium, then with sulfur leads to 1-butyl-3,4-dimethylphosphole sulfide. Similarly, the reaction of **1** with phenyllithium, then with sulfur gives 1-phenyl-3,4-dimethyl–phosphole sulfide in 50% isolated yield (Scheme 4). The monitoring of the reaction mixture after the addition of PhLi showed a single ^{31}P resonance at -8 ppm in THF. We suspected the formation of the η^4-anionic species **8**. This formulation was confirmed by the reaction of **8** with quaternizing agents giving the zwitterionic products **9** and **10** (Scheme 4).

In compound **9**, the α-CH protons appear as a doublet at 1.61 ppm ($^2J_{HP} = 18.4$ Hz). For **10**, the data are quite similar (δ_H 1.77 ppm, $^2J_{HP}$ 18.7 ppm) so, the complexation of the dienic system is clearly established. The X-ray crystal structure analysis of **9** (Fig. 1) shows that PhLi selectively attacks the phosphorus atom of **1** on the *exo* side. Other noteworthy features are a relatively weak P–Mn interaction at 2.765 Å and internal P–C (ring) bonds which are very short at 1.740–1.748(2) Å. It must be stressed here that (η^4-phosphonium)manganesetricarbonyl complexes were prepared for the first time by Lindner through a completely different approach [18]. Moreover, a similar reaction scheme has been shown to be at work during the reaction of ^{t}BuLi, then PhC(O)Cl with 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene [19].

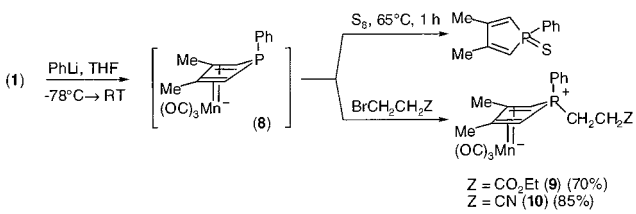
Without too much hope, we attempted to transpose this type of reaction with the 2-acetylphosphacy-



Scheme 2.



Scheme 3.



Scheme 4.

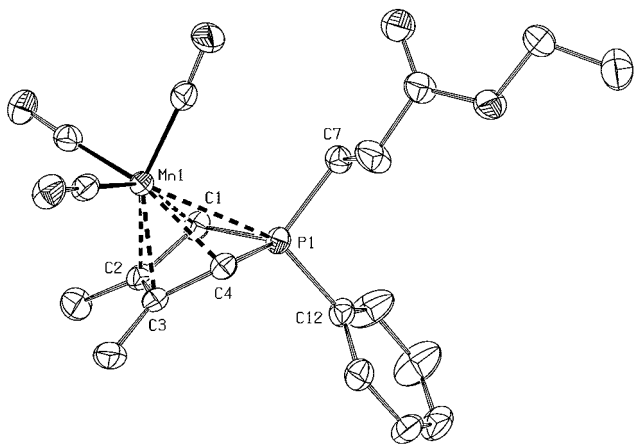


Fig. 1. Molecular structure of (**9**). Significant bond distances (Å) and angles (°): Mn(1)–C(1) 2.150(2), Mn(1)–C(2) 2.099(2), Mn(1)–C(3) 2.093(2), Mn(1)–C(4) 2.156(2), Mn(1)–P(1) 2.7651(8), P(1)–C(1) 1.740(2), P(1)–C(4) 1.748(2), P(1)–C(7) 1.814(2), P(1)–C(12) 1.819(2), C(1)–C(2) 1.447(3), C(2)–C(3) 1.414(3), C(3)–C(4) 1.449(3); C(1)–P(1)–C(4) 90.2(1), C(7)–P(1)–C(12) 103.6(1), C(1)–P(1)–C(7) 115.3(1), C(1)–P(1)–C(12) 116.5(1), C(4)–P(1)–C(7) 116.5(1), C(4)–P(1)–C(12) 115.2(1), C(1)–P(1)–Mn(1) 51.03(7), C(4)–P(1)–Mn(1) 51.25(7), C(7)–P(1)–Mn(1) 100.95(7), C(12)–P(1)–Mn(1) 155.45(7).

mantrene (**11**). The attack of **11** by a sub-stoechiometric amount of PhLi proved to be extremely clean. It gives a single product **12** with a ^{31}P resonance at -6 ppm in THF. Thus, the attack of **11** exclusively takes place at phosphorus, contrary to any reasonable expectation. This dramatically demonstrates the extraordinary electrophilicity of the phosphorus atom of **11** (Scheme 5).

The final product **13** displays all the expected spectral characteristics. The α-CH proton resonates at high field (δ_H 2.11 ppm, $^2J_{HP} = 16.0$ Hz), and the ketonic carbon appears at 202.78 ppm. Since this kind of η^4-phospholium complexes can be easily decomplexed [20] and dequaternized, we have here an unexpectedly clean and general method to recover phospholes from phosphacymantrenes.

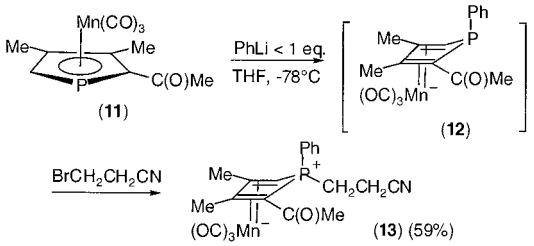
3. Experimental

3.1. General

All reactions were performed under an inert atmosphere (nitrogen or argon). NMR spectra were measured on a multinuclear Bruker 300 MHz spectrometer. Chemical shifts are expressed in ppm from internal TMS (^1H 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 analysis were performed at the service de Microanalyse du CNRS, Gif sur Yvette, France.

3.2. Photochemical decomplexation of phosphacymantrene (3)

2,5-Diphenylphosphacymantrene (**3**) (200 mg, 5.3×10^{-4} mol) was dissolved in 400 ml of a 1:1 mixture of diethyl ether and ethanol. The resulting solution was transferred into the irradiation cell and stirred with argon bubbling for 15 min, then submitted to UV irradiation for 75 min. The color of the solution quickly changed from light orange to dark red. Monitoring the reaction progress after 15 min by ^{31}P-NMR spectroscopy showed the complete disappearance of the starting material and the appearance of a single resonance at $\delta = -25$ ppm. No further evolution could then be detected. After the irradiation was stopped, the solvents were removed under vacuum. The resultant oil was redissolved in 5 ml of an hexane/diethyl ether (1:1) mixture and filtered through a pad of 1 cm of silica. The solvents were removed under vacuum to give the 2,2′,5,5′-tetraphenylbiphosphole (**4**) as a yellow oil (80 mg, 64% yield).



Scheme 5.

3.3. Reduction of phosphacymantrene (3) by naphthalene–lithium

2,5-Diphenylphosphacymantrene (**3**) (375 mg, 1×10^{-3} mol) was placed in a Schlenk tube under nitrogen atmosphere and 10 ml of distilled THF were added via a septum. Then, 20 ml of a 10^{-1} M naphthalene–lithium solution in THF were added in the same way. The orange solution slowly turned red. ^{31}P-NMR monitoring showed the complete consumption of **3** after 15 min and the appearance of two new resonances: the first one ($\delta = +78$ ppm) corresponding to the phospholide ion (**6**); the second one ($\delta = +3.5$ ppm; $J_{P-H} = 34$ Hz) unidentified. Addition of two equivalents of iodomethane (284 mg; 2×10^{-3} mol) resulted in a color change from red to orange; two products were detected by ^{31}P-NMR spectroscopy. They were isolated after evaporation of THF under reduced pressure and chromatography of the crude oil with silica gel and an hexane/diethyl ether mixture (9:1) as the eluent. The first product obtained was the 1-methyl-2,5-diphenylphosphole (**7**) (110 mg, 44% yield) and the second one was the starting 2,5-diphenylphosphacymantrene (**3**) (70 mg, 19% yield). Both products have been characterized by ^{31}P-, ^1H-, ^{13}C-NMR and mass spectroscopy.

3.4. Phospholium complexes

3.4.1. (η^4-1-Phenyl-1-(2-ethoxycarbonylethyl)-3,4-dimethylphospholium)tricarbonyl manganese (9)

To a solution of 3,4-dimethylphosphacymantrene (**1**) (0.5 g, 2×10^{-3} mol) in THF (10 ml) at -78 °C was added dropwise phenyllithium 1.7 M (1.25 ml, 2.12×10^{-3} mol). The mixture was allowed to warm to room temperature (r.t.) and treated with ethyl 3-bromopropionate (0.24 ml, 2×10^{-3} mol). After 30 min the solvent was removed and the residue extracted with dichloromethane, washed with water, dried with magnesium sulfate and purified by chromatography on silicagel with dichloromethane as the eluent; 0.6 g of **9** (70% yield) was obtained.

NMR ($CDCl_3$) ^1H: δ 1.13 (t, $^3J_{HH}$ 7.1 Hz, CH_2CH_3), 1.61 (d, $^2J_{HP}$ 18.4 Hz, Hα), 2.10 (s, Me), 2.55 (m, CH_2), 2.91 (m, CH_2), 3.99 (q, $^3J_{HH}$ 7.1 Hz, $COOCH_2$), 7.19–7.38 (m, Ph).^{13}C {^1H}: δ 14.63 (s, $COOCH_2CH_3$), 16.96 (d, $^3J_{CP}$ 6.2 Hz, CH_3), 22.04 (d, $^1J_{CP}$ 80.9 Hz, PCH_2),

25.79 (d, $^1J_{CP}$ 82.5 Hz, Cβ), 29.70 (d, $^2J_{CP}$ 3.3 Hz, CH_2COOEt), 61.83 (s, OCH_2), 94.68 (d, $^2J_{CP}$ 17.0 Hz, Cβ), 128.16 (d, $^2J_{CP}$ 10.6 Hz, C *ortho*), 129.62 (d, $^2J_{CP}$ 9.1 Hz, C *meta*), 131.99 (d, $^3J_{CP}$ 2.5 Hz, C *para*), 138.01 (d, $^1J_{CP}$ 12.5 Hz, C *ipso*), 172.08 (d, $^3J_{CP}$ 12.5 Hz, CH_2CO), 227.43 (Mn*C*O).^{31}P: δ 36.38.

Anal. Calc. for $C_{20}H_{22}O_5PMn$: C, 56.07; H, 5.14. Found: C, 55.82; H, 5.17%.

3.4.2. (η^4-1-Phenyl-1-(2-cyanoethyl)-3,4-dimethylphospholium)tricarbonylmanganese (**10**)

To a solution of 3,4-dimethylphosphacymantrene (**1**) (0.1 g, 0.4×10^{-3} mol) in THF (2 ml) at −78 °C, phenyllithium 1.7 M (0.25 ml, 0.425×10^{-3} mol) was added dropwise. The mixture was allowed to warm to r.t. and treated with 3-bromopropionitrile (0.033 ml, 0.4×10^{-3} mol). After 30 min the solvent was removed and the residue extracted with dichloromethane, washed with water, dried with magnesium sulfate and purified by chromatography on silicagel with dichloromethane as the eluent; 0.11 g of **10** (85% yield) was obtained.

NMR ($CDCl_3$) ^{1}H: δ 1.77 (d, $^2J_{HP}$ 18.7 Hz, Hα), 2.20 (s, CH_3), 2.79 (broad s,CH_2), 3.05 (broad s, CH_2), 7.27–7.52 (m, Ph). ^{13}C {^{1}H}: 13.64 (d, $^2J_{CP}$ 2.9 Hz, CH_2CN), 16.80 (d, $^3J_{CP}$ 6.0 Hz, CH_3), 23.56 (d, $^1J_{CP}$ 78.9 Hz, PCH_2), 24.61 (d, $^1J_{CP}$ 80.3 Hz, Cα), 94.83 (d, $^2J_{CP}$ 17.5 Hz, Cβ), 118.15 (d, $^3J_{CP}$ 12.6 Hz, CN), 127.94 (d, $^2J_{CP}$ 10.5 Hz, C *ortho*), 129.90 (d, $^3J_{CP}$ 9.3 Hz, C *meta*), 132.58 (s, C *para*), 136.99 (d, $^1J_{CP}$ 21.8 Hz, C *ipso*), 226.94 (s, CO). ^{31}P: δ 36.82.

Mass spectrum: *m*/*z* 297 ([M − 3CO], 19.5%), 242 ([M − Mn − 3CO]).

Anal. Calc. for $C_{18}H_{17}NO_3PMn$: C, 56.69; H, 4.46. Found: C, 56.93; H, 4.65%.

3.4.3. (η^4-1-Phenyl-1-(2-cyanoethyl)-2-acetyl-3,4-dimethylphospholium)tricarbonyl manganese (**13**)

To a solution of 2-acetyl-3,4-dimethylphosphacymantrene (**11**) (0.2 g, 0.68×10^{-3} mol) in THF (4 ml) at −78°C, phenyllithium 1.7 M (0.6 ml, 0.68×10^{-3} mol) was added dropwise. The mixture was allowed to warm to r.t. and treated with 3-bromopropionitrile (0.056 ml, 0.67×10^{-3} mol). After 30 min the solvent was removed and the residue extracted with dichloromethane, washed with water, dried with magnesium sulfate and purified by chromatography on silicagel with dichloromethane/ethyl acetate (95/5) as the eluent; 0.11 g of **13** (59% yield) was obtained.

NMR ($CDCl_3$) ^{1}H: δ 2.11 (d, $^1J_{HP}$ 16.0 Hz, HCP), 2.19 (d, $^4J_{HP}$ 1.1 Hz, CH_3), 2.28 (s, $COCH_3$), 2.38 (d, $^4J_{HP}$ 0.8 Hz, CH_3), 2.57–2.92 (m, CH_2), 3.05–3.30 (m, CH_2), 7.48–7.56 (m, Ph). ^{13}C {^{1}H} δ 13.46 (d, $^2J_{CP}$ 2.3 Hz, CH_2CN), 14.83 (d, $^3J_{CP}$ 3.7 Hz, CH_3), 18.03 (d, $^3J_{CP}$ 5.5 Hz, CH_3), 22.98 (d, $^1J_{CP}$ 77.4 Hz, Cα), 23.81 (d, $^1J_{CP}$ 78.9 Hz, PCH_2), 27.93 (d, $^3J_{CP}$ 7.7 Hz, $COCH_3$), 53.31 (d, $^1J_{CP}$ 87.7 Hz, Cα), 92.05 (d, $^2J_{CP}$ 23.1 Hz, Cβ), 99.86 (d, $^2J_{CP}$ 15.8 Hz, Cβ), 118.03 (d, $^3J_{CP}$ 13.8 Hz, CN), 129.89 (d, $^3J_{CP}$ 9.9 Hz, C *meta*), 129.93 (d, $^2J_{CP}$ 10.6 Hz, C *ortho*), 133.19 (d, $^4J_{CP}$ 2.5 Hz, C *para*); 133.53 (d, $^1J_{CP}$ 31.0 Hz, C *ipso*), 202.78 (broad s, $COCH_3$), 225.30 (s, MnCO). ^{31}P: δ 41.14.

Mass spectrum: *m*/*z* 423 ([M], 21.5%), 339 ([M − 3CO], 87.8%), 284 ([M − Mn − 3CO], 60.5%).

Anal. Calc. for $C_{20}H_{19}NO_4PMn$: C, 56.74; H, 4.49. Found: C, 56.85; H, 4.61%.

3.4.4. Crystallographic data for $C_{20}H_{22}MnO_5P$ (**9**)

$M = 428.29$ g mol^{-1}; monoclinic; space group $P2_1/c$; $a = 14.102(5)$ Å, $b = 17.354(5)$ Å, $c = 16.299(5)$ Å, $\beta = 92.350(5)°$, $V = 3985(2)$ Å^3; $Z = 8$, two identical molecules per asymmetric unit; $D_{calc} = 1.428$ g cm^{-3}; $\mu = 0.770$ cm^{-1}; $F(000) = 1776$. Crystal dimensions $0.20 \times 0.20 \times 0.20$ mm^3. Total reflections collected 18466 and 7510 with $I > 2\sigma(I)$. Goodness-of-fit on F^2 1.030; $R = 0.048$, $wR2 = 0.1205$ ($I > 2\sigma(I)$); $R = 0.0854$, $wR2 = 0.1377$(all data); maximum/minimum residual density 0.675(0.081)/ − 0.643(0.081) e Å^{-3}. Data were collected on a KappaCCD diffractometer at 150.0(1) K with Mo–K_α radiation ($\lambda = 0.71073$ Å).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 161737 for compound **9**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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References

[1] F. Mathey, A. Mitschler, R. Weiss, J. Am. Chem. Soc. 100 (1978) 5748.
[2] G. de Lauzon, B. Deschamps, J. Fischer, F. Mathey, A. Mitschler, J. Am. Chem. Soc. 102 (1980) 994.
[3] B. Deschamps, L. Ricard, F. Mathey, Organometallics 18 (1999) 5688.
[4] S. Qiao, G.C. Fu, J. Org. Chem. 63 (1998) 4168.
[5] K. Tanaka, S. Qiao, M. Tobisu, M.M.-C. Lo, G.C. Fu, J. Am. Chem. Soc. 122 (2000) 9870.
[6] C. Ganter, C. Kaulen, U. Englert, Organometallics 18 (1999) 5444.
[7] R. Shintani, M.M.-C. Lo, G.C. Fu, Org. Lett. 2 (2000) 3695.

[8] N.M. Kostic, R.F. Fenske, Organometallics 2 (1983) 1008.
[9] C. Guimon, G. Pfister-Guillouso, F. Mathey, Nouveau J. Chim. 3 (1979) 725.
[10] G. Keglevich, Z. Böcskei, G.M. Keserü, K. Ujszászy, L.D. Quin, J. Am. Chem. Soc 119 (1997) 5095.
[11] E. Deschamps, F. Mathey, Bull. Soc. Chim. Fr. 129 (1992) 486.
[12] E. Deschamps, L. Ricard, F. Mathey, Angew. Chem. Int. Ed. Engl. 33 (1994) 1158.
[13] S. Holand, M. Jeanjean, F. Mathey, Angew. Chem. Int. Ed. Engl. 36 (1997) 98.
[14] S. Holand, N. Maigrot, C. Charrier, F. Mathey, Organometallics 17 (1998) 2996.
[15] S. Top, E.B. Kabun, G. Jaouen, J. Am. Chem. Soc. 122 (2000) 736.
[16] DFT calculations have been performed on the parent complex $[Mn(\eta^5\text{-}C_4H_4P)(CO)_3]$ by P. Le Floch. Further details will be published later.
[17] C. Charrier, F. Mathey, Tetrahedron Lett. 28 (1987) 5025.
[18] E. Lindner, A. Rau, S. Hoehne, J. Organomet. Chem. 218 (1981) 41.
[19] B. Deschamps, J. Fischer, F. Mathey, A. Mitschler, L. Ricard, Organometallics 1 (1982) 312.
[20] B. Deschamps, J. Fischer, F. Mathey, A. Mitschler, Inorg. Chem. 20 (1981) 3252.