Facile Insertion of $ClPPh_2$ into Nb–H Bonds as a Synthetic Route to New Phosphino and Phosphido Derivatives of Niobocene

Georgii I. Nikonov* and Dmitry A. Lemenovskii*

Chemistry Department, Moscow University, Lenin Hills, 119899 Moscow, Russia

Jörg Lorberth*

Fachbereich Chemie, Philipps-Universität, Marburg, Hans-Meerwein-Strasse, D-35032 Marburg/Lahn, Germany

Received February 22, 1994®

Synthetic approaches to phosphorus derivatives of niobocene, including a metathesis of Cp_2NbH_2Li with $ClPPh_2$ and insertion of $ClPPh_2$ into the Nb–H bond, were studied. The smooth reaction of Cp'_2NbH_3 (**a**, Cp = C_5H_5; **b**, Cp′ = C_5H_4Me) with $ClPPh_2$ affords $[Cp'_2NbH_2PHPh_2]Cl$ (**3a,b**) in high yield. Deprotonation of **3** leads exclusively to $Cp'_2NbH(PHPh_2)$ (**2**), while the isomeric complex $Cp'_2NbH_2PPh_2$ (**1**) was not observed; it seems to be the intermediate precursor to complex **2**. Direct reaction of Cp_2NbH_2Li with $ClPPh_2$ also gives **2a** but in poorer yield. **2** was found to selectively rearrange into $Cp'_2Nb(PHPhC_6H_4–)$ (**5**), the first ortho-metalated phosphine complex of the early transition metals. The formulation of **5** was supported by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. However, X-ray diffraction study was not possible due to twinning problems. By repeated insertion of $ClPPh_2$ into the Nb–H bond of **2**, followed by deprotonation, we obtained $[Cp'_2Nb(PHPh_2)_2]Cl$ (**7**) and $(C_5H_4Me)_2NbPPh_2(PHPh_2)$ (**8b**). Deprotonation of **7** and **8b** affords a new niobocene anionic complex $Cp'_2Nb(PHPh_2)_2M$ (M = Na, Li (**9**)). Thermal degradation of **2**, **8**, and **9**, leading to **5**, was studied and found to proceed via an intermediate Cp'_2NbPPh_2 (**6**) which was identified by NMR spectroscopy.

Introduction

Phosphido derivatives of early transition metals have been intensively studied,[1–5] mainly as precursors to early/late heterobimetallic complexes (ELHB)[5] which are of potential interest as catalysts.[6] A wide variety of work has been done on the group 4 metallocenes,[1,2] while the group 5 phosphido complexes have been significantly less well documented.[3,4]

Our interest in phosphido-substituted metallocenes was initially stimulated by the recent studies on silicon and tin complexes of the formula $Cp_2MH_x(ER_3)_{3-x}$ (x = 1, 2; M = Nb, Ta; E = Si, Sn).[7,8] Investigation of corresponding phosphides would be of interest in order to compare properties of different element-substituted metallocenes. However, convenient synthetic routes to these complexes are lacking. Generally, there are three approaches to element-substituted metallocenes which have been applied to obtain phosphides: (1) the most common way of generating the M–E bond is by transmetalation[1,9,10] (eq 1a or eq 1b), the latter equation being

$$L_nM–Hal + M'ER_m \rightarrow L_nM–ER_m + M'Hal \quad (1a)$$

$$L_nM–M' + HalER_m \rightarrow L_nM–ER_m + M'Hal \quad (1b)$$

less applicable because of the poorly developed chemistry of the organometallic anions $(L_nM)^-$ [1n,11,12] of the

® Abstract published in *Advance ACS Abstracts*, July 1, 1994.

(1) (a) Ellerman, J.; Poersch, P. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 335. (b) Issleib, K.; Hackert, H. *Z. Naturforsch.* **1966**, *21B*, 519. (c) Baker, R. T.; Whitney, J. F.; Wreford, S. S. *Organometallics* **1983**, *2*, 1049. (d) Wade, S. R.; Wallbridge, M. G. H.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1983**, 2555. (e) Weber, L.; Meine, G.; Boese, R.; Augart, N. *Organometallics* **1987**, *6*, 2484. (f) Pagne, R.; Hachgene, J.; Fritz, G.; Fenske, D. *Z. Naturforsch.* **1986**, *41B*, 1535. (g) Chang, M. Y.; Gambarotta, S.; Bolhuis, F. V. *Organometallics* **1988**, *7*, 1864. (h) Benac, B. L.; Jones, R. A. *Polyhedron* **1989**, *8*, 177. (i) Baker, R. T.; Krusic, P. J.; Tulip, T. H.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 6763. (j) Roddick, D. M.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4670. (k) Hey, E.; Bott, S. G. Atwood, J. L. *Chem. Ber.* **1988**, *121*, 561. (l) Dick, D. G.; Stephen, D. W. *Can. J. Chem.*, **1991**, *69*, 1146. (m) Dick, D. G.; Stephan, D. W. *Organometallics* **1991**, *10*, 2811. (n) Ho, J.; Drake, R. J.; Stephan, D. W. *J. Am. Chem. Soc.* **1993**, *115*, 3792. (o) Hou, Z.; Stephan, D. W. *J. Am. Chem. Soc.* **1992**, *114*, 10088. (p) Hou, Z.; Breen, T. L.; Stephan, D. W. *Organometallics* **1993**, *12*, 1358.

(2) (a) Ho, J.; Stephan, D. W. *Organometallics* **1992**, *11*, 1014 and literature therein. (b) Ho, J.; Stephan, D. W. *Organometallics* **1991**, *10*, 3001. (c) Ho, J.; Hou, Z.; Drake, R. J.; Stephan, D. W. *Organometallics* **1993**, *12*, 3145.

(3) (a) Bonnet, G.; Lavastre, O.; Leblanc, J.-C.; Moise, C. *New J. Chem.* **1988**, *12*, 551. (b) Bonnet, G.; Kubicki, M. M.; Moise, C.; Lazzaroni, R.; Salvador, P.; Vitulli, G. *Organometallics* **1992**, *11*, 964.

(4) Ol'dekop, Yu. A.; Knizhnikov, V. Z. *Zh. Obshch. Chem.* **1981**, *51*, 723.

(5) (a) Stephen, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41 and literature therein. (b) Baker, R. T.; Fultz, W. C.; Marder, T. B.; Williams, I. D. *Organometallics* **1990**, *9*, 2357.

(6) (a) Senocq, F.; Randrianalimanana, C.; Thorez, A.; Kalck, P.; Cloukroun, R.; Gervais, D. *J. Mol. Catal.* **1986**, *35*, 213. (b) Choukroun, R.; Gervais, D.; Kalck, P.; Senocq, F. *J. Organomet. Chem.* **1987**, *335*, C.9. (c) Choukroun, R.; Gervais, D.; Jaud, J.; Kalck, P.; Senocq, F. *Organometallics* **1986**, *5*, 67. (d) Gelmini, L.; Stephen, D. W. *Organometallics* **1988**, *7*, 849. (e) Kalck, P.; Serra, C.; Machet, C.; Broussier, R.; Gautheron, B.; Delmas, G.; Trouve, G.; Kubicki, M. *Organometallics* **1993**, *12*, 1021. (f) Larsonneur, A.-M.; Choukroun, R.; Daran, G.-C.; Cuenca, T.; Flores, J. C.; Royo, P. *J. Organomet. Chem.* **1993**, *444*, 83. (g) Recent application of Ta/Ir ELHB see: Hostetler, M. J.; Butts, M. D.; Bergman, R. G. *Organometallics* **1993**, *12*, 65.

(7) (a) Jiang, Q.; Carrol, P. J.; Berry, D. H. *Organometallics* **1991**, *10*, 3648. (b) Curtis, M. D.; Bell, L. G.; Buter, N. M. *Organometallics* **1985**, *4*, 701.

(8) Green, M. L. H.; Hughes, A. K.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1991**, 1407.

(9) Woo, H.-G.; Freeman, W. P.; Tilley, T. D. *Organometallics* **1992**, *11*, 2198.

(10) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, G. J. *Organometallics* **1987**, *6*, 473 and literature therein.

0276-7333/94/2313-3127$04.50/0

early transition metals; (2) oxidative addition of $H-ER_m$ to an electron-deficient metal center (eq 2) is suitable

$$L_nM + HER_m \rightarrow L_nM(H)ER_m \qquad (2)$$

for the preparation of silicon[7,13-15] and tin[8] derivatives, but usually gives poor yields when applied to phosphides;[1p,2,16] (3) insertion of an electron-deficient main-group element moiety into the M—H bond[17-19] (eqs 3a and 3b) has not so far been used for synthesis of

$$L_nMH + ER_m \rightarrow L_nM-EHR_m \qquad (3a)$$

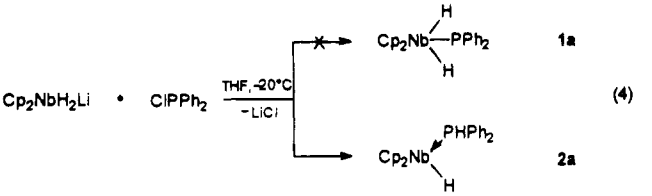
$$L_nMH + XER_m \rightarrow L_nM-ER_m + HX \qquad (3b)$$

phosphides. Some examples of the S_N2 substitution at phosphorus by a basic organometallic moiety, closely related to (1b), have also been reported.[3,20]

Here, we report our results on the application of methods (1b) and (3b) to a synthesis of new phosphino and phosphido derivatives of niobocene. The main feature of these studies is that the hydride phosphine complex $Cp_2NbH_2PPh_2$ (**1**), independent of its synthesis, very easily rearranges into its isomer $Cp_2Nb(HPPh_2)H$ (**2**). The latter exhibits a wealth of reactivity and was used for the syntheses of a number of other phosphorus-containing niobocenes.

Results

1. Reaction of Cp_2NbH_2Li with $ClPPh_2$. Cp_2NbH_2Li[11b,21] is an easily accessible reagent for introduction of the Cp_2NbH_2 moiety and a precursor for the phosphido complex $Cp_2NbH_2PPh_2$ (**1a**). Accordingly, Cp_2NbH_2Li was reacted with 1 equiv of $ClPPh_2$ in THF (eq 4). In an analogous reaction of Cp_2NbH_2Li with $ClSnMe_3$, the tin complex $Cp_2NbH_2SnMe_3$[11b] was obtained in high yield. Surprisingly, in the case of $ClPPh_2$, no trace of the expected phosphido complex **1** was



(4)

observed. Instead, the hydride phosphine complex **2a** was formed in 30% yield. The structure of **2a** was unequivocally proven by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. **2a** had been discovered earlier as one of the products of the thermal degradation of Cp_2NbH_3 in the presence of $HPPh_2$.[22] However, the unexpected low yield of **2a** at that time was not fully understood, considering the fact that the analogous reaction of Cp_2NbH_3 with tertiary phosphines to form complexes $Cp_2NbH(PR_3)$ proceeds with high yield.[23]

2. Reaction of Cp_2NbH_3 with $ClPPh_2$. The insertion of tin halides into M—H bonds[18,19] prompted us to study analogous insertion reactions of $ClPPh_2$. The reaction of Cp'_2NbH_3 with $ClPPh_2$ proceeds smoothly, yielding quantitatively the ionic complex $[Cp'_2NbH_2(PHPh_2)]Cl$ (**3**)[24] as depicted in eq 5. **3** is immediately

$$Cp'_2NbH_3 + ClPPh_2 \xrightarrow[-10 \text{ to } -20°C]{\text{toluene}} \underset{\textbf{3a,b}}{(Cp'_2NbH_2(HPPh_2))Cl} \qquad (5)$$

a, $Cp' = C_5H_5$; **b**, $Cp' = C_5H_4Me$

precipitated as white, voluminous flakes when toluene solutions of Cp'_2NbH_3 and $ClPPh_2$ are mixed at −20 °C. **3** is very sparingly soluble in hydrocarbon, ethereal, and aromatic solvents; however, it is sufficiently soluble in acetone, methanol, and water to obtain NMR spectra. The suggested structure of **3** was supported by ^1H, ^{13}C, and ^{31}P NMR spectra, and subsequent chemical derivatizations.

In the ^1H NMR spectrum of **3a** (methanol-d_4), only the symmetric isomer $Cp_2NbH_2PHPh_2Cl$ was observed. Cp ring protons of **3a** exhibit a slightly broadened doublet at δ 5.57 ppm (J_{P-H} = 1.0 Hz), shifted to low field with respect to the corresponding signals of **2**.[22] The hydrogen atom of the P—H bond is displayed as a broad signal at δ 6.2 ppm (a half of the doublet; the second half is hidden in the signals of the phenyl groups). The broad shape of this signal may result from an internal exchange reaction or be caused by a hydrogen exchange reaction with the solvent (vide infra). The Nb—H hydride signal is observed at δ −1.75 ppm. The resonance is split due to coupling with phosphorus (J_{P-H} = 75.8 Hz) and P—H proton (J_{P-H} = 3 Hz).

A proton exchange reaction with the solvent was also observed in the ^1H NMR spectrum of **3a**: on standing, the P—H proton signal disappears along with the H—H coupling of the Nb—H signal and there is a simultaneous increase in the intensity of the residual MeOH-d_3. In contrast, the intensity of the Nb—H resonance perfectly corresponds to the Cp signal in the ratio 2:10.

(11) (a) Hitchcock, P. B.; Lappert, M. F.; Leung, W. P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282. (b) Green, M. L. H.; Hughes, A. K.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1991**, 1699.

(12) Tueting, D. R.; Olmstead, M. M.; Schore, N. *Organometallics* **1992**, *11*, 2235 and literature therein.

(13) Addition of H—SiR to group 4–6 metallocenes and its application in catalysis see: Aitken, C.; Barry, J.-P.; Ganvin, F.; Harrod, J. F.; Malek, A.; Roussean, D. *Organometallics* **1989**, *8*, 1732 and literature therein.

(14) Addition of $H-SiR_3$ to the group 4 metallocenes see: (a) Aitken, C.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* **1986**, *64*, 1647. (b) Correy, J. V.; Zhu, X.-Y. *Organometallics* **1992**, *11*, 672. (c) Kesti, M. R.; Waymouth, R. M. *Organometallics* **1992**, *11*, 1095. (d) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rouset, C. J.; Fanwick, F. E.; Nigishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8565.

(15) Addition of $H-SiR_3$ to group 5 metallocenes see ref 7 and also: Berry, D. H.; Koloski, T. S.; Carrol, P. J. *Organometallics* **1990**, *9*, 2952.

(16) (a) Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *Organometallics* **1989**, *8*, 1760. (b) Nielsen-Marsh, S.; Growte, R. J.; Edwards, R. G. *J. Chem. Soc., Chem. Commun.* **1992**, 699. (c) Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1982**, *1*, 1332.

(17) Berry, D. H.; Jiang, Q. *J. Am. Chem. Soc.* **1987**, *109*, 6210.

(18) Skripkin, V. V.; Volkov, O. G.; Pasynskii, A. A.; Antsyshkina, A. S.; Dikareva, L. M.; Ostikova, V. N.; Porai-Koshits, M. A.; Davydova, S. L.; Sakharov, S. G. *J. Organomet. Chem.* **1984**, *263*, 345.

(19) (a) Arkhireeva, T. M.; Bulychev, B. M.; Protsky, A. N.; Soloveichik, G. L.; Bel'sky, V. K. *J. Organomet. Chem.* **1986**, *317*, 33. (b) Protsky, A. N.; Bulychev, B. M.; Soloveichik, G. L.; Bel'sky, V. K. *Inorg. Chim. Acta* **1986**, *115*, 121.

(20) (a) Kubicki, M. M.; Kergoat, R.; Cariou, M.; Guerchais, J. E.; L'Haridon, P. *J. Organomet. Chem.* **1987**, *322*, 357. (b) Barre, C.; Kubicki, M. M.; Leblanc, J.-C.; Moise, C. *Inorg. Chem.* **1990**, *29*, 5244.

(21) Lemenovskii, D. A.; Nifant'ev, I. E.; Perevalova, E. G.; Timofeeva, T. V.; Slovokhotov, Yu. L.; Struchkov, Yu. T. *J. Organomet. Chem.* **1986**, *342*, 31.

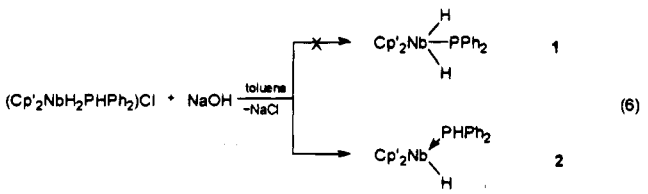
(22) Leblanc, J.-C.: Moise, C. *J. Organomet. Chem.* **1989**, *364*, C3.

(23) (a) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 3793. (b) Barefield, E. K.; Parshall, G. W.; Tebbe, F. N. *J. Am. Chem. Soc.* **1970**, *92*, 5234.

(24) Throughout this paper index **n** denotes both **na** and **nb** (n = 1, 2, 3,..), **a** refers to normal Cp compounds and **b** to their Me-substituted cyclopentadienyl analogoues.

This observation clearly demonstrates that the P—H bond is considerably weaker than the Nb—H bond and it is the phosphorus proton which is involved in the exchange reaction.

Corresponding complexes of the type $Cp_2NbH_2(PR_3)Cl$ are well-known;[25] they are easily obtained by treatment of $Cp_2NbH(PR_3)$ with HCl and can be quantitatively deprotonated by NaOH, affording the starting material. A characteristic feature of **3** is the availability of two acidic centers: at the Nb—H and P—H bonds. However, treatment of **3** with aqueous NaOH in toluene gives only **2** in ~70% yield; again the phosphido complex **1** is not observed (eq 6).



(6)

It should be noted that the homologous tantalum complex $Cp_2TaH_2(PPh_2)$ was mentioned[22] earlier, but neither characterization nor description of its synthesis was reported. Our investigation led us to assume that **1** is not stable and, even if it is formed, rapidly converts into the much more stable complex **2**.

The cationic complex **3** is somewhat thermally sensitive: for example, keeping a colorless suspension of **3a** in toluene at room temperature for 8–10 days results in the gradual formation of a brown solution of $Cp_2NbCl(HPPh_2)$ (**4a**), which was eventually isolated as large brown crystals in high yield.

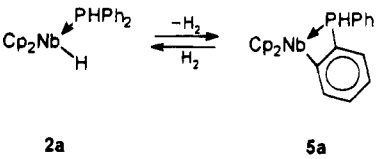
$$2Cp_2NbH_2(HPPh_2)Cl \xrightarrow{8-10\ \text{days}} Cp_2NbCl(HPPh_2) + H_2 \quad (7)$$

The ^1H NMR spectrum of **4a** (toluene-d_8) shows three groups of signals: Cp protons were observed as a doublet (δ 4.67 ppm, J_{P-H} = 2.4 Hz) shifted to a lower field with respect to the Cp signal of **2a**.[26] The P—H proton displays a doublet at δ 6.55 ppm (J_{P-H} = 337.6 Hz) in the range characteristic for other diphenylphosphine complexes: **2** and $(C_5H_4Me)_2NbPPh_2(HPPh_2)$ (vide infra). Phenyl groups give rise to complex multiplets in the aromatic region; no protons of the Nb—H moiety were observed.

The presence of two other products in low concentrations was also indicated by the ^1H NMR spectrum of **4a**. The first was identified as the free phosphine $HPPh_2$ by comparison with an authentic sample; the second impurity, indicated by a singlet at δ 4.70 ppm, was assigned as $(Cp_2NbCl)_2$.[27] On heating the NMR sample of **4a** to 60 °C, both concentrations increased. It is quite feasible that these impurities arise from the dissociation of **4a**:

$$2Cp_2NbCl(HPPh_2) \xrightarrow{60\ °C} (Cp_2NbCl)_2 + 2HPPh \quad (8)$$

3. Thermolysis of $Cp_2NbH(HPPh_2)$. On standing under ambient conditions, **2a** stepwise loses dihydrogen, but no phosphine, selectively yielding a new phosphorus-containing compound **5a** (eq 9). This process was



(9)

2a **5a**

monitored by NMR spectroscopy. The reaction is reversible, but it takes about 2 weeks to reach equilibrium at room temperature in the NMR sample. Heating the resulting mixture at 60 °C for 2 h does not significantly change the ratio **2**:**5**. Raising the temperature to 80 °C results in the significant degradation to form bis(niobocene)[23a] and a number of unidentified compounds.

The ^1H and ^{13}C NMR spectra of **5a** can be rationalized in terms of an ortho-metalated phenyl group of the coordinated phosphine.[28] Thus, in the ^1H NMR spectrum of **5a** (toluene-d_8) we observed a signal attributed to the P—H proton (δ 6.53 ppm, J_{P-H} = 315 Hz), but no Nb—H hydride was observed up to −30 ppm. The Cp protons give rise to two closely located doublets at δ 4.42 ppm (J_{P-H} = 1.5 Hz and J_{P-H} = 1.6 Hz), caused by the nonequivalence of the Cp groups and proton—phosphorus coupling. The asymmetric phosphorus center results from the formation of the metallacycle, hindering the rotation about the Nb—P bond. In contrast, the ^{13}C NMR spectrum displays only one Cp ring singlet at 92.21 ppm.

Thermolysis of **2a** in THF, with periodic removal of dihydrogen, allowed us to prepare **5a** quantitatively (by NMR). A toluene solvate of **5a** was isolated in 67% yield as large red crystals by cooling the saturated toluene–heptane (1:1) solution. Ten crystals were investigated for an X-ray study, but none of them was suitable due to twinning. Recrystallization from Et_2O afforded **5a** as long red needles. However, again all of them were twinned. Thermolysis of **2b** was carried out analogously, but all attempts to crystallize **5b** by cooling its saturated solutions failed.

In spite of the lack of precise structural information, we are confident in the formulation of **5a** as a phosphine ortho-metalated product. An alternative bimetallic structure $[Cp_2Nb(\mu\text{-}PHPhC_6H_4-)]_2$ should be rejected, because one can expect its Cp signal position in the ^{13}C NMR spectrum and its phosphorus NMR signal to be close to those of **2a**, the only complex of the type $Cp_2Nb(R)PR_3$[23a,25a] (R = Alk, H) for which ^{13}C and ^{31}P NMR spectroscopic data are available. In contrast, **5a** displays quite different data: 92.21 ppm versus 83.38 ppm and 60.8 ppm versus 2.0 ppm, correspondingly. The low-field phosphorus signal of **5a** (60.8 ppm) is especially conclusive for the interpretation of a four-membered

(25) (a) Lucas, C. R.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1972**, 2005. (b) Leboeuf, J.-F.; Lavastre, O.; Leblanc, J.-C.; Moise, C. *J. Organomet. Chem.* **1991**, *418*, 359.

(26) In the related complex $Cp_2Nb(PMePh_2)Cl$, Cp ring resonances were found at δ 4.67 (d, J_{P-H} = 1.8 Hz): Tueting, D. R.; Olmstead, M. M.; Schore, N. E. *Organometallics* **1992**, *11*, 2235.

(27) Lemenovskii, D. A.; Baukova, T. V.; Fedin, V. P. *J. Organomet. Chem.* **1977**, *132*, C14.

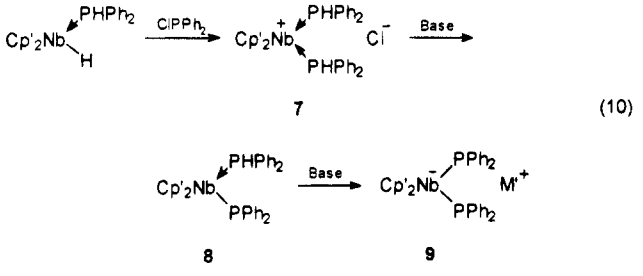
(28) Other examples of C—H activation in the alkyl or aryl moiety of coordinated phosphine see: (a) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139. (b) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (c) Omae, I. *Coord. Chem. Rev.* **1980**, *32*, 235. (d) Rathke, J. W.; Muetterties, E. I. *J. Am. Chem. Soc.* **1975**, *97*, 3272. (e) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *107*, 3929. (f) Jung, J. W.; Fellmann, J. D.; Garrou, P. *Organometallics* **1983**, *2*, 1042, (g) C—H activation in a phosphinidene derivative of zirkonocene see ref 1p.

metallacycle: it is well-known that chelated phosphorus complexes exhibit considerable ^{31}P chemical shifts in comparison with their acyclic analogues.[28b]

Thermolysis of **2a** to **5a** occurs via an intermediate **6a** which arises in the NMR spectra of *initially pure* **2a** after storing the NMR sample. However, there are no signals of **6a** in the NMR spectra of *crude* **5a** obtained by heating of **2a** with removal of dihydrogen, indicating that **6a** is a real intermediate rather than a byproduct. In the ^1H NMR spectrum, **6a** displays a Cp proton signal as a doublet at 4.62 ppm (J_{P-H} = 2.1 Hz), indicating coupling with one phosphorus atom. No hydride and P—H proton signals were observed. Phenyl proton resonances of **6a** cannot be assigned, since they are in the bulk of the signals for **2a** and **5a**; however, they contribute to the overall intensity in this region. Its Cp ring signal in the ^{13}C NMR spectrum (92.25 ppm) is close to that of **5a**, reflecting the electronic deficiency of the niobocene moiety, as compared with the starting electron-rich complex **2a** (83.38 ppm). On the basis of these data, we assign **6a** a monophosphido structure Cp_2NbPPh_2. Further confirmation of this 16-electron phosphido species can be deduced from the low-field shifted ^{31}P resonance of **6a** (51.0 ppm), indicating a partial π-donation from phosphorus to a vacant orbital of the niobocene moiety.[29]

To the best of our knowledge, this is the first example of phosphine ortho-metalation in the chemistry of the early transition metals. Earlier, Gell and Schwartz[30] suggested C—H bond activation in the phenyl ring of coordinated phosphine in the solution of Cp_2ZrPPr_2Ph, but again, this product was neither isolated nor characterized. Recently, Harrod et al. have reported an intramolecular C—H activation of the PMe_3 group in the silyl phosphine complex $Cp_2Ti(PMe_3)SiHR_2$ to form $Cp_2Ti(PMe_2CH_2—)$. However, arguments for this formulation were provided only on the basis of ESR spectra.[31]

4. Preparation of Phosphido and Phosphine Complexes of Niobocene. The synthesis of phosphides of the type $Cp_2Nb(L)PR_2$,[3] and their use in the preparation of ELHB, inspired us to use **2** for the synthesis of its phosphido derivatives, and their subsequent use as organometallic ligands, carrying out the following reaction sequence:



(a: Cp' = C_5H_5, M' = Li, b: Cp' = C_5H_4Me, M' = Na)

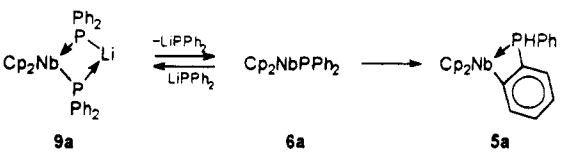
Every step of this process proceeds smoothly, and each complex can be isolated in high yield. **7** was obtained in the form of an orange powder, stable in air for some minutes. **8b** can be isolated only in the form of air-sensitive, oily crystals even after repeated crystallization from ether. This is caused by its thermal instability to phosphine dissociation: on standing at room temperature **8b** converts stepwise to complex **5b** (eq 11). Signals of **5b** and free phosphine $HPPh_2$ can

$$Cp'_2NbPPh_2(HPPh_2) \rightarrow \mathbf{5} + HPPh_2 \qquad (11)$$

be identified in the ^1H and ^31P NMR spectra even of freshly prepared samples of **8b**. The structure of **8b** was assigned on the basis of ^1H, ^{13}C, and ^{31}P NMR spectroscopy and by comparison with related complexes of the type $(Cp)_2Nb(PPh_2)PR_3$.[3a] No signals of isomeric $(C_5H_4Me)_2Nb(PPh_2)_2H$ were found.

Deprotonation of **8** to **9** proceeds quantitatively on treatment with *n*-BuLi or $NaN(SiMe_3)_2$.[32] The anionic complex $(C_5H_4Me)_2Nb(PPh_2)_2Na{\cdot}nEt_2O$ was isolated in crystalline form on standing of a concentrated toluene solution. The preparation of a versatile organometallic synthon as a precursor to ELHB, $Cp_2Nb(PR_2)_2^-$ (**9a**), can be effectively performed in a one-pot reaction by treatment of **2a** with $ClPPh_2$, followed by deprotonation with excess *n*-BuLi in pentane.

In contrast to $(C_5H_4Me)_2Nb(PPh_2)_2Na$, $Cp_2Nb(PPh_2)_2$-Li is not indefinitely stable: in the ^1H NMR spectrum of the lithium compound some degradation products were found, the main product being **5**. It is likely that Li^+ forms a stronger bond with the PPh_2 moiety than Na^+, providing dissociation according to eq 12.



(12)

Stephen et al.[1m] have recently reported an analogous equilibrium for a titanocene complex on the basis of its ESR spectrum:

$$Cp_2TiPR_2 + LiPR_2 \rightleftarrows Cp_2Ti(PR_2)_2Li \qquad (13)$$

Discussion

Reaction of $Cp_2Nb(L)H$ with $ClPPh_2$, affording $[Cp_2Nb(L)PHPh_2]Cl$, was previously rationalized[3a] in terms of S_N2 substitution at phosphorus by the metal centered lone pair of $Cp_2Nb(L)H$. Some related processes were also found in the molybdocene chemistry.[20] We have found that Cp_2NbH_3, lacking a lone pair, smoothly reacts with $ClPPh_2$, demonstrating that chlorophosphines (formally d-acids) can themselves easily insert into the Nb—H bond (formally σ-base). These two competitive mechanisms are depicted in Scheme 1.

The nature of the insertion process is not quite clear, but can be considered as an interaction of empty

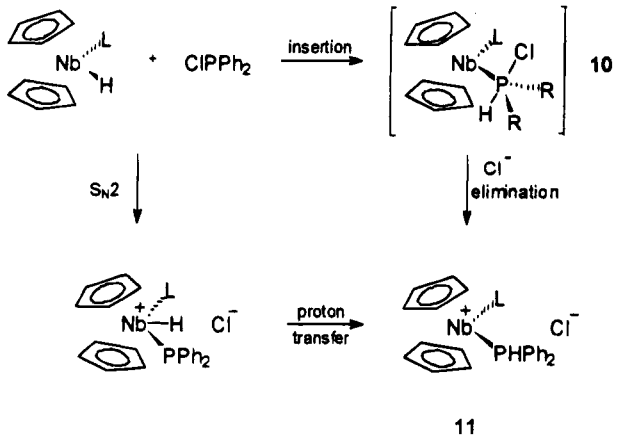
(29) The diphenylphosphido ligand in **6** is unable to adopt the geometry required for effective π-donation because this would require the two Ph group to be directed toward the Cp ring. Effective P→M π-donation in phosphido derivatives of metallocenes is known to cause a large downfield shift of the phosphido group signal in the ^{31}P spectrum (202–270 ppm),[1c,1j] whereas the 18-electron phosphides lacking π-donation exhibit high-field signals in the −10 to −50 ppm region,[1c] depending on the nature of the complex. Partial donation causes a downfield shift of intermediate value (30–90 ppm).[16a]

(30) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687.

(31) Woo, H. G.; Harrod, J. F.; Henique, J.; Samuel, E. *Organometallics* **1993**, *12*, 2883.

(32) The same idea in order to prepare an anionic phosphido complex via deprotonation of coordinated HPR_2 was earlier successfully applied for the synthesis of dianions $[LM(PR_2)_2]^{2-}$ (M = Mo, W): (a) Johansen, G.; Stelzer, O. *Chem. Ber.* **1977**, *110*, 3448. (b) Stelzer, O.; Under, E.; Wray, V. *Chem. Ber.* **1977**, *110*, 3430. (c) Targos, T. S.; Rosen, R. P.; Whittle, R. R.; Geoffroy, G. L. *Inorg. Chem.* **1985**, *24*, 1375.

Scheme 1

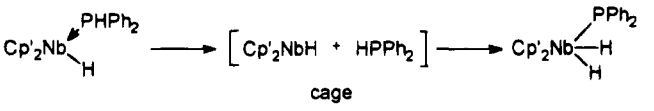


d-orbitals at phosphorus with the Nb—H σ-bond. The structure with pentavalent phosphorus (like **10** in Scheme 1) should be initially formed, but cannot be detected. Probably, it rapidly converts to the cationic phosphine complex (like **11** in Scheme 1) via elimination of the chloride ion, or it may be only a transition state. At present, we cannot differentiate between S_N2 substitution or an insertion mechanism for $Cp_2Nb(L)H$. The former is more feasible from an electronic point of view, since the lone pair of $Cp_2Nb(L)H$ is its HOMO lying above the Nb—H σ-bond orbital. The latter, however, seems to be more favorable from steric considerations, since this lone pair is more shielded by the Cp ligands than the Nb—H bond.

In the case of the reaction between Cp'_2NbH_3 and $ClPPh_2$, the initial product is a cationic complex **3**, which can be considered either as a quaternary phosphonium salt or as a protonated hydride phosphine complex **2**. The first description, however, seems to be more operative since the P—H proton was found to be much more labile than the Nb—H proton. This implies that deprotonation of **3** should initially produce dihydride phosphine complex **1** which, however, cannot be detected and, probably, rapidly transforms into **2** via a hydride shift into the vacant d-orbital at phosphorus.

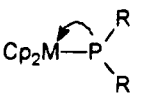
Further, though also indirect, evidence for the intermediancy of **1** follows from the selective transformation of **2** to **5**. It is highly unlikely that the elimination of dihydrogen from **2** proceeds directly, since the large activation barrier, caused by the van der Waals repulsion of the Nb—H and P—H bonds, would have to be overcome. In contrast, elimination of dihydrogen from a metal complex is a common reaction and the asymmetric isomer of **1** (**1'**) is a reasonable candidate for this process (Scheme 2).

Reverse formation of **1'** from **2** cannot now be considered as a hydride shift, since there is no suitable vacant orbital in the metal in **2**, but may occur via $HPPh_2$ dissociation, followed by the P—H bond activation, as shown in eq 14.[33]



(14)

Elimination of dihydrogen from **1'** affords a 16-electron monophosphido complex of the type **12**, which is somewhat stabilized by partial π-donation of the phosphorus lone pair to the metallocene vacant orbital,



12

as deduced from the ^{31}P resonance signal position of **6**. However, for the early transition metal monophosphido complexes, this kind of stabilization is not strong enough to permit their isolation, and an additional stabilizing factor is necessary. For example, titanocene monophosphido derivatives are known only as adducts with THF, e.g. $Cp_2TiPR_2{\cdot}THF$, and on standing they gradually transform into dimers $[Cp_2Ti(\mu\text{-}PR_2)]_2$ (**13**).[1a,b,g,l] In the case of **6** we have found another way of stabilization: ortho-metalation of the phenyl ring of the phosphine occurs, affording **5**.

Why does Cp_2TiPR_2 afford the dimer **13**, and **6** only a mononuclear species **5**? We assume that it is the metal—metal bond in **13** which provides dimerization, while for the niobium dimer $Cp_2Nb(\mu\text{-}PR_2)_2NbCp_2$ it would not be possible. Moreover, in the latter case we can expect steric hindrance approximately similar to that in **8**, providing facile elimination. Thus *intramolecular* stabilization happens to be the preferred reaction.

Conclusion

Although the initial goal of this study, to prepare phosphido complexes of the type $Cp_2NbH_x(PR_2)_{3-x}$ (x = 1, 2), was not achieved, we have found a convenient entry to some phosphorus-substituted niobocenes, based on direct insertion of chlorophosphine into the Nb—H bond of niobocene, giving ionic phosphine complexes $[Cp_2Nb(HPR_2)X]Cl$ (X = H_2, $HPPh_2$). The P—H bond present in the coordinated phosphine reveals additional reaction pathways in comparison with related PR_3 derivatives. Two different approaches (1b) and (3b) surprisingly yield the same product $Cp_2Nb(HPPh_2)H$ (**2**); its isomer $Cp_2NbH_2PPh_2$ was not observed but, probably, is formed as a transient intermediate. The preference of $Cp_2Nb(HPPh_2)H$ versus $Cp_2NbH_2PPh_2$ and $Cp_2Nb(PPh_2)HPPh_2$ versus $Cp_2Nb(PPh_2)_2H$ is more likely to be governed by thermodynamic factors, and we believe that modification of phosphorus substituents, influencing both Nb—P and P—H bonds, could reverse this situation.

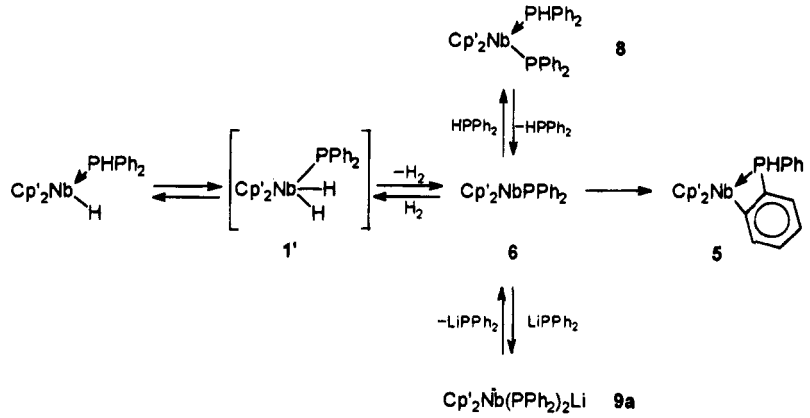
2 is a reactive species and readily eliminates H_2, affording $Cp_2Nb(PHPhC_6H_4-)$, the first example of an early transition metal phosphine complex with an ortho-metalated phenyl group. The identical product results from the thermal decomposition of $(C_5H_4Me)_2Nb(HPPh_2)PPh_2$ and $Cp_2Nb(PPh_2)_2Li$ (**9**).

(33) A number of other hydrogen transfer processes from nitrogen or phosphorus to a metal center are known; all of them give, as an intermediate, M=N[34] or M=P[1b] double bonds. Apart from this, an equilibrium $H—M—NH_3 \rightleftarrows (H_2)M—NH_2$ was observed for an iridium complex.[35] All these reactions proceed for coordinatively unsaturated complexes.

(34) (a) Walsh, P. J.; Carney, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *105*, 6343. (b) Nikonov, G. I.; Putala, M.; Zinin, A. I.; Kazennova, N. B.; Lemenovskii, D. A.; Batsanov, A. S.; Struchkov, Yu. T. *J. Organomet. Chem.* **1993**, *452*, 87.

(35) Koelliner, R.; Milstein, D. *J. Am. Chem. Soc.* **1991**, *113*, 8524.

Scheme 2



Finally, we have described a convenient synthesis of a prospective precursor **9** to the phosphido metalloligand for the preparation of ELHB.

Experimental Section

Cp_2NbCl_2[36] and Cp'_2NbCl_2 were obtained in an atmosphere of dry argon. A minor modification of the literature method was used to obtain Cp'_2NbCl_2.[7b]: $NbCl_4$·THF instead of $NbCl_5$ was treated with 2 equiv of $Cp'SnMe_3$ in CH_2Cl_2 (yield 80–90%). All other operations were carried out in vacuo using conventional Schlenk techniques.

Cp_2NbH_3 and Cp'_2NbH_3 were prepared by the literature method[7b] using Et_2O as a solvent and $LiAlH_4$ as the reducing agent. This gives white trihydrides in pure form in yields up to 70%. There is no need to sublime the complex as in the case of $NaH_2Al(OCH_2CH_2OCH_3)_2$.[7b] $ClPPh_2$ was purchased from Merck.

Toluene was distilled from Na/K alloy, and Et_2O and THF were distilled from sodium benzophenone ketyl. The ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer operating at 400 and 100.4 MHz, respectively. The ^1H chemical shifts were referenced to the residual protonated solvent. The $^{31}P\{^1H\}$ NMR spectra were recorded on an FT-80A Varian spectrometer, and phosphorus chemical shifts are reported relative to 85% H_3PO_4. IR spectra were obtained with a IKS-26 spectrometer. Elemental analyses were performed in the analytical laboratory of the Chemistry Department of Moscow University.

(1) a. Preparation of $[Cp'_2NbH_2(PHPh_2)]Cl$ (3b). Cp'_2NbH_3, obtained from 1.855 g of Cp'_2NbCl_2 (5.76/mmol), was treated with 15 mL of an ethereal solution of 1.1 mL of $ClPPh_2$ (6.13/mmol). A white precipitate was immediately formed. When sedimentation was completed, the colorless solution was decanted, the residue washed twice with 10 mL of Et_2O and dried in vacuo. Yield: 1.566 g (62%) based on Cp'_2NbCl_2. IR (Nujol): ν_{P-H} = 2250 cm^{-1} (broad), ν_{Nb-H} = 1700 cm^{-1}. ^1H NMR (acetone-d_6): δ 7.39–7.20 (m, 10, Ph groups), 6.6 (broad, half of a doublet, 0.5, P–H), 5.14 and 4.80 (broad singlets, 8, C_5H_4Me), 1.84 (s, 6, Me), −1.80 (doublet, J_{P-H} = 38 Hz, Nb–*H*). ^{31}P NMR (acetone-d_6): δ 19.90 ppm (broad). Anal. Calcd for $C_{24}H_{27}ClPNb$: C, 60.71; H, 5.73. Found: C, 61.15; H, 6.58.

b. Preparation of $Cp_2NbH_2PHPh_2Cl$ (3a). **3a** was obtained analogously to **3b** by treatment of 0.8 g (3.54 mmol) of Cp_2NbH_3 with an excess of $ClPPh_2$. Yield: 1.1 g (2.46 mmol, 69.6%). IR (Nujol): ν_{P-H} = 2260 cm^{-1} (broad), ν_{Nb-H} = 1700 cm^{-1}. ^1H NMR (methanol-d_4): δ 7.69–7.50 (m, 10, Ph groups), 6.20 (broad, half of a doublet, 0.5, P–*H*), 5.66 (doublet, J_{P-H} = 1.0 Hz, 10, Cp), −1.75 (dd, J_{P-H} = 75.8 Hz and $^3J_{H-H}$ = 3 Hz, Nb–*H*). ^{13}C NMR (methanol-d_4): δ 133.01, 132.89, 131.66, 129.86, 129.73 (Ph), 94.72 (Cp). ^{31}P NMR (methanol-d_4): δ 17.0 ppm. Anal. Calcd for $C_{22}H_{24}ClPNb$: C, 59.15; H, 5.19. Found: C, 58.82; H, 4.93.

(2) a. Preparation of $Cp'_2Nb(HPPh_2)H$ (2b). $Cp'_2Nb(HPPh_2)H_2Cl$ (1.566 g, 3.56 mmol) was added to a mixture of 20 mL of a 0.5 M aqueous solution of NaOH and 50 mL of toluene, and the solution was vigorously stirred. Within some minutes the powder dissolves and the organic layer turns dark red. The toluene solution was decanted and the solvent removed in vacuo. The red residue was recrystallized from Et_2O, yielding 0.960 g (67%) of $Cp'_2NbH(HPPh_2)$. ^1H NMR (toluene-d_8): δ 7.63, 7.08–6.96 (m, 10, Ph), 6.82 (d, J_{P-H} = 319.2 Hz, 1, P–H), 4.36, 4.27, 4.25, 4.11 (m, 8, C_5H_4Me), 1.96 (s, 6, Me), −6.99 (doublet, J_{P-H} = 24.8 Hz, Nb–*H*). ^{31}P NMR (toluene-d_8): δ 9.1 ppm. Anal. Calcd for $C_{24}H_{26}ClPNb$: C, 65.76; H, 5.98. Found: C, 65.53; H, 5.66.

b. Preparation of $Cp_2Nb(HPPh_2)H$ (2a). $Cp_2Nb(HPPh_2)H$ was prepared by the same procedure as **2b** from 1.1 g (2.46 mmol) of $[Cp_2NbH_2(PHPh_2)]Cl$. Yield: 0.535 g (1.315 mmol, 53%). ^1H NMR (toluene-d_8): δ 7.567, 7.117–6.968 (m, 10, Ph), 6.727 (d, J_{P-H} = 321.6 Hz, 1, P–H), 4.406 (d, J_{P-H} = 2.5 Hz, 10, Cp). ^{13}C NMR (toluene-d_8): 83.376 (Cp). ^{31}P NMR (toluene-d_8): δ 2.0 ppm. Anal. Calcd for $C_{22}H_{22}NbP$: C, 64.40; H, 5.40. Found: C, 64.03; H, 5.27.

(3) Preparation of $Cp_2Nb(HPPh_2)Cl$ (4a). Cp_2NbH_3 (1.161 g, 5.13 mmol) was treated with 1 mL (5.57 mmol) of $ClPPh_2$ in 20 mL of toluene to form a white precipitate of **3a**. The mixture was left for 12 days. The solution gradually became brown, and a brown crystalline substance was formed. The toluene solution was concentrated to 5 mL and decanted. The residue obtained was recrystallized from toluene, washed with cold ether (5 mL), and dried in vacuo, yielding 1.452 g of large brown crystals (3.27 mmol, 63.6%). IR (Nujol): ν_{P-H} = 2270 cm^{-1} (broad). ^1H NMR (toluene-d_8): δ 7.45, 7.32, 7.00 (m, 10, Ph), 6.55 (d, J_{P-H} = 378 Hz, 1, P–H), 4.67 (d, $J_{P_5bd_H}$ = 2.4 Hz, 10, Cp). ^{13}C NMR (toluene-d_8): δ 95.21 (Cp). ^{31}P NMR (toluene-d_8): δ 51.32 ppm. Anal. Calcd for $C_{22}H_{21}NbCl$: C, 59.41; H, 4.76. Found: C, 58.19; H, 4.97.

(4) a. Preparation of $Cp_2Nb(HPPhC_6H_4-)$ (5a). **2a** (0.274 g, 0.668 mmol) was dissolved in 10 mL of THF and heated for h at 50 °C with periodic removal of H_2. The solvent was removed in vacuo, and the red residue was dissolved in toluene–heptane (1:1). Cooling to −20 °C resulted in the formation of large well-shaped crystals, the toluene solvate of **5a**. Yield: 0.226 g (0.452 mmol, 67.6%). ^1H NMR (toluene-d_8): δ 7.41, 7.19, 7.12–6.97 (m, 9, Ph and C_6H_4), 6.53 (d, J_{P-H} = 315 Hz, 1, P–*H*), 4.424 (d, J_{P-H} = 1.5, 5, Cp), 4.421 (d, J_{P-H} = 1.6 Hz, 1, Cp). ^{13}C NMR (toluene-d_8): δ 92.21 (Cp). ^{31}P NMR (toluene-d_8): δ 61.1. Anal. Calcd for $C_{29}H_{28}NbP$: C, 69.61; H, 5.64. Found: C, 69.60; H, 5.65.

b. Preparation of $Cp'_2Nb(HPPhC_6H_4-)$ (5b). **5b**, pure from **2b** (NMR checked), was obtained in the same manner. However, we failed to isolate **5b** in crystalline, analytically

(36) Hitchcock, P. B.; Lappert, M. F.; Milne, Ch. R. C. *J. Chem. Soc., Dalton Trans.* **1981**, 180.
(37) Labinger, J. A.; Wong, K. S. *J. Organomet. Chem.* **1979**, *170*, 373.

pure form because of the high solubility of **5b** in common organic solvents. ^{1}H NMR (benzene-d_6): δ 7.60, 7.35, 6.93 (m, 9, Ph), 5.81 (half of a doublet, 0.5, P—*H*), 4.56, 4.22, 4.13, 4.06 (broad, 8, C_5H_4Me), 1.49 (s, 6, Me). ^{13}C NMR (benzene-d_6): δ 109.66, 97.71, 93.42, 89.66, 89.16 (C_5H_4Me), 14.83 (Me). ^{31}P NMR (benzene-d_6): δ 63.8 (**5b**), 20.9 (**6b**).

(5) a. Preparation of $Cp'_2Nb(HPPh_2)_2Cl$ (7b). $Cp'_2Nb(HPPh_2)H$ (0.679 g, 1.55 mmol) was mixed with 0.45 mL (2.5 mmol) of $ClPPh_2$ in 30 mL of Et_2O at room temperature. An orange powder was immediately formed; sedimentation was completed within some minutes. The almost colorless solution was decanted and the residue was washed with 25 mL of Et_2O and dried in vacuo. Yield: 0.867 g (1.32 mmol, 85%). ^{1}H NMR (acetone-d_6): δ 7.52–7.31 (m, 20, Ph), 5.20 (d, J_{P-H} = 217.7 Hz, P—*H*), 5.34 and 4.71 (m, 8, C_5H_4Me), 1.874 (s, 6, Me). Anal. Calcd for $C_{36}PNbCl$: C, 65.62; H, 5.51. Found; C, 66.18; H, 5.95.

b. Preparation of $Cp_2Nb(HPPh_2)_2Cl$ (7a). The Preparation was analogous to **7b**. Yield: 91%. ^{1}H NMR (methanol-d_4): δ 7.48–7.31 (m, 20, Ph), 6.19 (broad, half of a doublet, 1, P—*H*), 5.07 (s, 10, Cp). ^{13}C NMR (methanol-d_4): 133.47, 131.17, 129.96, 129.90 (Ph), 93.54 (Cp). Anal. Calcd for $C_{34}H_{32}ClPNb$: C, 64.73; H, 5.11. Found: C, 64.40; H, 4.97.

(6) Preparation of $Cp'_2Nb(HPPh_2)PPh_2$ (8b). A solution of 0.872 g (3.25 mmol) of Cp'_2NbH_3 in 2 mL of toluene was mixed with a solution of 1.25 mL (6.96 mmol) of $ClPPh_2$ and 1 mL (7.2 mmol) of NEt_3 in 4 mL of toluene. An orange precipitate was immediately formed. On standing for some days, the orange powder gradually dissolves and the solution turns brown. Decantation followed by removal of the solvent in vacuo affords a red-brown residue. Recrystallization from Et_2O gives red oily crystals. Yield: 0.360 g (0.606 mmol) of **8b**, 18% based on Cp'_2NbH_3. We failed to obtain **8b** in an analytically pure form even after repeated recrystallization because of thermal decomposition. ^{1}H NMR (toluene-d_8): δ 7.48, 7.32 (m, 20, Ph), 6.41 (broad doublet, 326 Hz, 1, P—*H*), 4.61, 4.30, 4.18, 4.09 (broad singlets, 8, C_5H_4Me), 1.62 (s, 6, Me). ^{13}C NMR (toluene-d_8): δ 109.61, 97.53, 93.18, 89.54, 88.96 (C_5H_4Me), 14.69, 14.60 (C_5H_4Me). ^{31}P NMR (toluene-d_8): δ 19.2 ($HPPh_2$), −15.1 (PPh_2); (admixture signals) δ 61.0 ($Cp'_2Nb(HPPhC_6H_4-)$), −41.5 ($HPPh_2$).

(7) a. Preparation of $Cp'_2Nb(PPh_2)_2Na$ (9b). To 20 mL of an ethereal solution of $Cp'_2Nb(HPPh_2)PPh_2$ (0.360 g, 0.606 mmol) was added 1 mL of a 0.91 M Et_2O solution of $NaN(SiMe_3)_2$; the initial red solution turned brown. Solvent was removed in vacuo and the residue was dissolved in 3 mL of toluene, giving an oil. Standing at room temperature for 2 days resulted in the formation of dark red crystals. The viscous solution was decanted, and the residue was washed with a small amount of cold toluene and dried in vacuo. NMR spectra revealed the presence of a toluene solvate. Yield: 0.211 g (0.297 mmol, 49%). ^{1}H NMR (THF-d_8): δ 7.49 (m, 8, Ph), 6.87 (m, 8, Ph), 6.67 (m, 4, Ph), 7.20–7.09 (m, C_6H_5Me), 4.33 and 3.84 (8, C_5H_4Me), 2.31 (s, 3, C_6H_5Me), 1.62 (s, 6, C_5H_4-Me). ^{13}C NMR (THF-d_8): δ 95.54 and 89.80 (C_5H_4Me), 21.49 (C_6H_5Me), 14.94 (C_5H_4Me). ^{31}P NMR (THF-d_8): δ 33.1. The extremely high sensitivity of **9b** to air prevented reliable elemental analyses.

b. Preparation of $Cp_2Nb(PPh_2)_2Li$ (9a). $Cp_2Nb(HPPh_2)_2Cl$ (0.562 g, 0.890 mmol) was suspended in 30 mL of Et_2O and treated with 3 mL of 1.8 N BuLi in hexane. The solution turned from colorless to brown, and the precipitate gradually changed color from orange to brown on standing overnight. The solution was decanted, and the powder was washed twice with 10 mL of *n*-hexane and dried in vacuo. Yield: 423 g (0.704 mmol, 79%). ^{1}H NMR (THF-d_8): δ 7.51 (m, 8, Ph), 6.86 (m, 8, Ph), 6.84 (m, 4, Ph), 4.24 (s, 10, Cp).

Acknowledgment. G.I.N. and D.A.L. thank The Russian Foundation for Fundamental Investigations for partial support of this work. G.I.N. also gratefully acknowledges support through the "Hochschulsonderprogramm HSP2" of the County of Hessen, Germany, for an extended research grant during 1993/94, Philipps-University at Marburg, Germany, for providing ample research facilities.

OM940135B