Synthesis, Structure, and Deprotonation of a Mesitylphosphido-Bridged Cyclopentadienylnickel(II) Dimer

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The bridging phosphido complex $[NiCp(\mu\text{-}PHMes)]_2$ (**1**, Mes = 2,4,6-$Me_3C_6H_2$) was prepared from $NiCp_2$ and PH_2Mes. Deprotonation and methylation of **1** yields $(NiCp)_2(\mu\text{-}PHMes)(\mu\text{-}PMeMes)$ (**4**) and $[NiCp(\mu\text{-}PMeMes)]_2$ (**6**) via observable anionic phosphinidene intermediates. NMR spectroscopy was used to characterize syn and anti isomers of **1**, **4**, and **6**, and the structures of anti-**1a** and syn-**6b** were determined by X-ray crystallography.

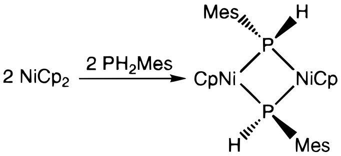
Introduction

Many dinuclear metal complexes with bridging secondary phosphido (μ-PR_2) ligands are known,[1] but the corresponding μ-PHR primary derivatives are less common.[2] Such complexes contain reactive P−H bonds and may be used as precursors to phosphinidene ligands.[3] We report here the preparation of a mesitylphosphido-bridged Ni(II) cyclopentadienyl complex and its deprotonation to generate anionic μ-phosphinidene species, which are characterized by ^{31}P NMR and by their reactions with methyl iodide.

Results and Discussion

Treatment of nickelocene with PH_2Mes (Mes = 2,4,6-$Me_3C_6H_2$) in petroleum ether gives a brown solution which deposits $[NiCp(\mu\text{-}PHMes)]_2$ (**1a**) as shiny brown air-stable crystals in 70−80% yield (Scheme 1). Several other phosphorus-containing products are formed. The major one, which shows a ^{31}P NMR signal at δ −68.6 (d, $^1J_{PH}$ = 211 Hz), may be a (mesitylphosphino)-cyclopentene derivative, since $NiCp_2$ and $HP(CF_3)_2$ give the analogous secondary phosphido complex $[NiCp\{\mu\text{-}P(CF_3)_2\}]_2$ and bis((trifluoromethyl)phosphino)cyclopentene.[4] We did not, however, attempt to characterize these byproducts further.

Scheme 1



1a

Complex **1a** was characterized spectroscopically. The ^{31}P NMR spectrum (CD_2Cl_2) shows an 8-line pattern at δ −237. Spectral simulation of the AA′XX′ spin system[5] gives $^2J_{PP}$ = 432.6 Hz, $^1J_{PH}$ = 318.3 Hz, $^3J_{PH}$ = −20.5 Hz, and $^4J_{HH}$ = 5.3 Hz. These coupling constants are similar to those reported[6] for $[NiCp(\mu\text{-}PH_2)]_2$, which are shown along with ^{31}P NMR data for other complexes reported here in Table 1. The P−H protons give rise to an identical pattern (δ 3.62, CD_2Cl_2) in the ^1H NMR spectrum, but only the more intense four middle lines are observed. The presence of P−H bonds is also evident from the IR spectrum (ν_{PH} = 2323 cm^{-1}, KBr). Deuterium-labeled **1D** was prepared from PD_2Mes. Its ^2H NMR spectrum could be simulated using coupling constants (Table 1) obtained from the results for **1a** and the gyromagnetic ratios[7] γ_H/γ_D = 6.5144. The IR spectrum of **1D** shows ν_{PD} = 1688 cm^{-1} (ν_{PH}/ν_{PD} = 1.38).

The anti configuration of the mesityl groups in **1a**, expected sterically, was confirmed by X-ray crystallography (Figure 1). Crystal, data collection, and refinement parameters are given in Table 2. Atomic coordinates and equivalent isotropic displacement coef-

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Table 1. ^{31}P NMR Data for Nickel μ-Phosphido and μ-Phosphinidene Dimers[a]

compd	$\delta(^{31}\mathrm{P})$	$^2J_{\mathrm{PP}}$	$^1J_{\mathrm{PH}}$ ($^1J_{\mathrm{PD}}$)
$[\mathrm{NiCp}(\mu\text{-PH}_2)]_2$[b]	−305	440	303
anti-$[\mathrm{NiCp}(\mu\text{-PHMes})]_2$ (**1a**)[c]	−237	432.6	318.3 (48.9)
syn-$[\mathrm{NiCp}(\mu\text{-PHMes})]_2$ (**1b**)[d]	−220.2	364.9	326.8
$[\mathrm{M}][(\mathrm{NiCp})_2(\mu\text{-PHMes})(\mu\text{-PMes})]$ (**2**)[e]	−94.2, −150.8[f]	198	296 (45.8)
$\mathrm{Li}_2[\mathrm{NiCp}(\mu\text{-PMes})]_2$ (**3**)[g]	13.8		
anti-$(\mathrm{NiCp})_2(\mu\text{-PHMes})(\mu\text{-PMeMes})$ (**4a**)[h]	−168.4, −223.6[f]	425.6	315 (48.4)
syn-$(\mathrm{NiCp})_2(\mu\text{-PHMes})(\mu\text{-PMeMes})$ (**4b**)[i]	−153.7, −212.2[f]	373.8	318 (48.9)
$[\mathrm{M}][(\mathrm{NiCp})_2(\mu\text{-PMes})(\mu\text{-PMeMes})]$ (**5**)[e]	−56.9, −99.3	198	
anti-$[\mathrm{NiCp}(\mu\text{-PMeMes})]_2$ (**6a**)[i]	−168		
syn-$[\mathrm{NiCp}(\mu\text{-PMeMes})]_2$ (**6b**)[i]	−154.6		

[a] Chemical shifts are reported in ppm (85% H_3PO_4 external reference) and coupling constants in Hz. [b] $^3J_{\mathrm{PH}} = -18$: Schafer, H.; Zipfel, J.; Migula, B.; Binder, D. *Z. Anorg. Allg. Chem.* **1983**, *501*, 111−120. [c] In CD_2Cl_2; $^3J_{\mathrm{PH}} = -20.5$; $^4J_{\mathrm{HH}} = 5.3$. For **1D**, $^3J_{\mathrm{PD}} = -3.1$ and $^4J_{\mathrm{DD}} = 0.8$. [d] In CD_2Cl_2; $^3J_{\mathrm{PH}} = -9.4$; $^4J_{\mathrm{HH}} = 3.0$. [e] In THF, M = Na or Li. [f] Peak showing $^1J_{\mathrm{PH}}$ ($^1J_{\mathrm{PD}}$). [g] In THF. [h] In C_6D_6; $|^3J_{\mathrm{PH}}| = 17$. [i] In C_6D_6.

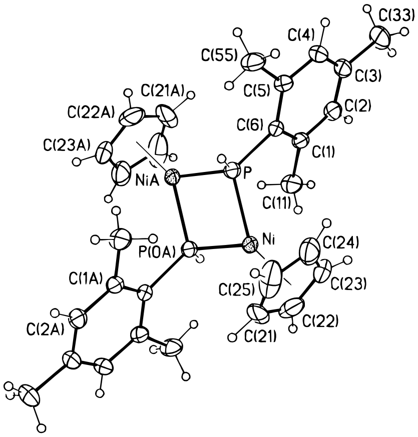

Figure 1. ORTEP diagram of **1a**, with thermal ellipsoids at 35% probability. Selected bond lengths (Å): Ni−P 2.158(2); Ni−P_a 2.152(2); Ni_a−P 2.152(2); Ni···Ni_a 3.340(2); Ni−Cnt 1.740(5); P−H 1.257(44); P−C(6) 1.827(6). Selected bond angles (deg): P−Ni−P_a 78.4(1); Ni−P−C(6) 121.4(2); Ni−P−Ni_a 101.6(1); C(6)−P−Ni_a 114.8(2); Ni−P−H 105.7(6); H−P−C(6) 106.3(6).

Table 2. Crystallographic Data for *anti*-$[\mathrm{NiCp}(\mu\text{-PHMes})]_2$ (1a) and *syn*-$[\mathrm{NiCp}(\mu\text{-PMeMes})]_2\cdot0.5$(pentane) ($\mathbf{6b}\cdot0.5C_5H_{12}$)

	1a	$\mathbf{6b}\cdot0.5C_5H_{12}$
formula	$C_{28}H_{34}Ni_2P_2$	$C_{35}H_{50}Ni_2P_2$
fw	539.8	650.1
space group	$P2_1/c$	$C2/c$
a, Å	11.831(6)	16.724(3)
b, Å	13.353(5)	13.576(2)
c, Å	8.613(4)	27.494(4)
β, deg	104.27(4)	92.55(1)
V, Å^3	1319(1)	6236(2)
Z	2	8
cryst color	red-brown	brown
D(calc), g cm^{-3}	1.385	1.384
μ(Mo Kα), cm^{-1}	15.62	13.33
temp, K	296	243
radiation	Mo Kα (λ = 0.710 73 Å)	
$R(F)$, %	5.38[a]	6.67[b]
$R(\mathrm{w}F)$, %	6.62[a]	16.24[b,c]

[a] Quantity minimized = $\sum w\Delta^2$; $R = \sum\Delta/\sum(F_o)$; $R(\mathrm{w}) = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$. [b] Quantity minimized = $R(\mathrm{w}F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$. [c] $R(\mathrm{w}F^2)$, %.

ficients are given in the Supporting Information. Selected bond lengths and angles appear in the figure caption; full listings are available as Supporting Information. The Ni−P bond lengths and PNiP angles are similar to those in $[\mathrm{NiCp}(\mu\text{-PPh}_2)]_2$[8] [for this complex, Ni−P = 2.15(0.7) Å, Ni−P′ = 2.16(0.8) Å, and the PNiP angle is 77.6(2)°] despite the different cone angles of PH_2Mes and $PHPh_2$ (110 and 128°, respectively).[9] The P−H protons were located and refined. The phosphido P atom is roughly tetrahedral; the relevant angles are Ni−P−H 105.7(6)°, H−P−C(Mes) 106.3(6)°, Ni−P−Ni 101.6(1)°, and Ni−P−C(Mes) 121.4(2)°. The last of these values is presumably larger for steric reasons.

The ^{1}H NMR spectrum of **1a** provides evidence for restricted rotation about the P−C bonds at room temperature. The two ortho methyls of a mesityl group are inequivalent and appear as broad signals at 3.29 and 2.43 ppm (CD_2Cl_2). The aryl protons give two broad, overlapping signals from 6.84 to 6.75 ppm. At −20 °C these peaks are sharp and well-resolved, and the ^{13}C{^{1}H} NMR spectrum shows six different signals for the mesityl ring carbons, consistent with slow rotation about the P−C bond on the NMR time scale at this temperature. In toluene-d_8 the ^{1}H NMR Ar signals coalesce at ~30 °C and the *o*-Me ones at ~60 °C. More precise data could not be obtained because of isomerization of **1a** on warming (see below); these observations give a rotational barrier of ~15 kcal/mol.[10] Related restricted rotations about N−C bonds in $[\mathrm{Ni}(\mathrm{C_5Me_4R'})(\mu\text{-NHR})]_2$ complexes were reported very recently.[11]

On standing in solution, **1a** undergoes partial isomerization to *syn*-$[\mathrm{NiCp}(\mu\text{-PHMes})]_2$ (**1b**); an apparent equilibrium mixture of ~5:1 **1a**:**1b** is formed in THF or CD_2Cl_2 (Chart 1).[12] Complex **1b** is characterized by its ^{31}P NMR spectrum (Table 1), which is similar to that of **1a** but with a reduced $^2J_{\mathrm{PP}}$ and a less shielded ^{31}P chemical shift. The expected P−H ^{1}H NMR signal for **1b** can also be observed (δ 4.20 in CD_2Cl_2), as can a new signal from its Cp protons (δ 4.73). However, the chemical shifts of its mesityl protons and methyl groups cannot be distinguished from those of **1a** at room temperature.

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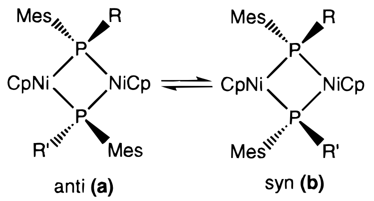
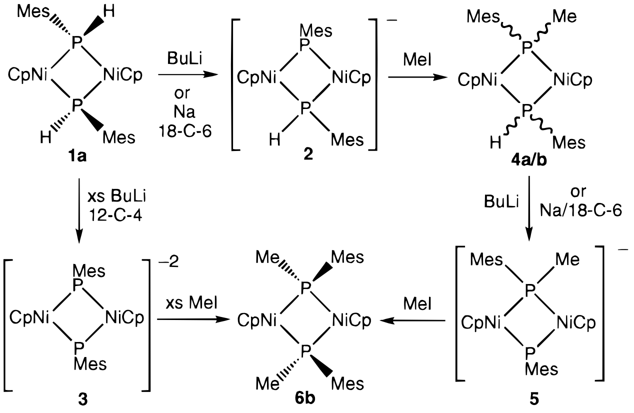
Chart 1



1a/b R = R' = H
4a/b R = H, R' = Me
6a/b R = R' = Me

Scheme 2



Deprotonations of μ-PHR groups have been reported for a variety of metal complexes,[3,12bc,13] and similar results were observed for **1** (Scheme 2). Reaction of **1a** or a mixture of **1a/b** with n-BuLi or t-BuLi in THF at room temperature generates Li[(NiCp)$_2$(μ-PHMes)(μ-PMes)] (**2**). Its ^{31}P NMR spectrum shows two doublet signals at δ −94.2 and −150.8 ($^2J_{PP}$ = 198 Hz); the latter peak shows an additional $^1J_{PH}$ of 296 Hz and is assigned to the phosphido P, while no $^3J_{PH}$ is observed for the phosphinidene P. The reduced $^2J_{PP}$ observed on formation of **2** from **1** can be rationalized by increased s character in the P lone pair orbital of **2**; similar changes in ^{31}P chemical shifts and coupling constants have been reported for related anions.[14] Deprotonation of **1D** gave **2D**, which shows $^1J_{PD}$ = 45.8 Hz.

With an excess of base and longer reaction times, a signal at 13.8 ppm, which shows no P−H coupling, is observed; this peak is assigned to the dianion Li$_2$[NiCp-(μ-PMes)]$_2$ (**3**). Complex **3** could be generated selectively, free of **2**, by deprotonation of **1a** in THF with an excess of *n*-BuLi in the presence of 12-crown-4.

Treatment of **1a** with an excess of sodium metal and 18-crown-6 in THF (the reaction was slower without the crown ether) selectively gives anion **2**. We assume that this reaction proceeds, as reported[15] for [NiCp(μ-PPh$_2$)]$_2$, by formation of a radical anion, which loses a hydrogen atom to yield the observed product.

We did not attempt to isolate or further characterize spectroscopically anions **2** or **3**; instead their reactions with methyl iodide were investigated. Anion **2** could be selectively methylated to form (NiCp)$_2$(μ-PHMes)(μ-PMeMes) (**4**, Scheme 2) as an ~4:1 mixture of anti (**4a**) and syn (**4b**) isomers (Chart 1), which were isolated as a brown petroleum-ether-soluble solid whose IR spectrum shows a P−H stretch at 2303 cm^{-1} (KBr). The inequivalent P nuclei in **4a** give rise to two doublets ($^2J_{PP}$ = 425.6 Hz) at δ −168.4 and −223.6; the latter shows an additional $^1J_{PH}$ of 315 Hz, while the former shows an unresolved multiplet due to coupling with the P−H and the P−Me protons. Related observations are made for **4b**, with chemical shift and coupling constant differences between syn and anti isomers similar to those observed for **1a/b**. (Table 1). Methylation of **2D** gives isomers **4D**.

The mixture of isomers **4a**,**b** is most easily differentiated in the ^{1}H NMR spectrum by their P−Me resonances, which show coupling to one or both of the P nuclei. The P−H resonance could be seen for **4a** (δ 4.16, dd, $^1J_{PH}$ = 314, $|^3J_{PH}|$ = 17 Hz in toluene-d_8), but the corresponding peak for **4b** was not observed due to its low intensity. At 22 °C in toluene-d_8, **4b** shows two resonances (δ 3.00, 2.82) due to the ortho methyl protons of its Mes groups, while **4a** shows only one at δ 3.04 (6H). At −60 °C, new ortho-Me signals due to **4a** [δ 3.32 (3H), 2.43 (3H)] which are unobserved at room temperature, grow in, along with new peaks due to the Mes ring protons [δ 6.76 (1H), 6.54 (1H)]. The spectrum of **4b** is unaffected by these temperature changes. From these observations, it appears that, as in **1a**, there is restricted rotation about the P−C bond in anti isomer **4a**.

Further deprotonation of **4a/b** with *n*-BuLi or Na/18-crown-6 gives the anion M[(NiCp)$_2$(μ-PMeMes)(μ-PMes)] (**5**; M = Li, Na; Table 1). The $^2J_{PP}$ of 198 Hz in **5** is identical to that in anion **2**, and the changes in ^{31}P chemical shifts on deprotonation are also consistent with the results for **1** and **2**. As with **2** and **3**, complex **5** was not further characterized or isolated. Treatment with MeI (Scheme 2) gives the symmetrical dimer [NiCp(μ-PMeMes)]$_2$ (**6**), which is also formed (in low yield) in the direct reaction of dianion **3** with methyl iodide. Analysis of reaction mixtures by ^{31}P NMR (Table 1) suggests that both anti and syn isomers **6a**,**b** (Chart 1) are formed (the assignments were made on the basis of the chemical shift trends observed for **1a**/**b** and **4a**/**b**), but this mixture converts to pure **6b** over the course of 1 day.

No P−H resonance is observed in the IR spectrum of isolated **6b**. In the ^{1}H NMR spectrum, the P−Me protons give rise to a triplet at 1.01 ppm (C$_6$D$_6$). Such apparent triplet splitting has been reported previously[16] for complexes with bridging methylphosphido groups and attributed to strong P−P coupling, as observed for **1** and **4**. The peak separation gives the average P−H coupling of the methyl protons to the two phosphorus nuclei. The observed value of 6 Hz is consistent with the average of these couplings directly measured for **4b** ($^2J_{PH}$ = 10.2, $^4J_{PH}$ = 2 Hz).

Hindered rotation of a mesityl group is characteristic of the anti isomers **1a** and **4a**. Because this phenomenon is not observed in the ^{1}H NMR spectrum of **6b**, the isomer observed in solution is likely to be the syn one, consistent with the assignment based on the ^{31}P NMR chemical shift discussed above. The crystal structure of **6b** (Figure 2) confirms this geometry in the

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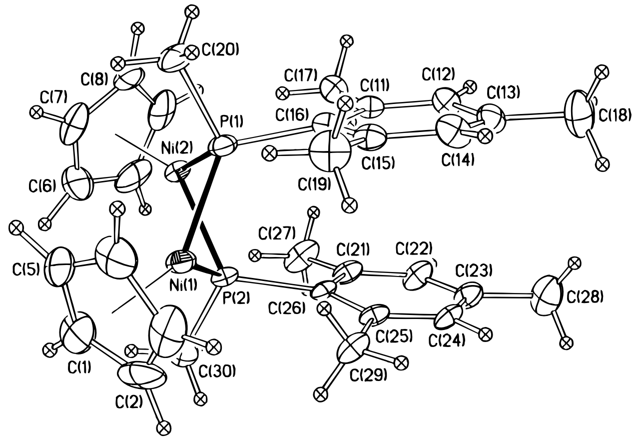

Figure 2. ORTEP diagram of **6b**, with thermal ellipsoids at 35% probability. Selected bond lengths (Å): Ni(1)−P(1) 2.168(2); Ni(1)−P(2) 2.164(3); Ni(2)−P(1) 2.161(3); Ni(2)−P(2) 2.167(2); Ni(1)···Ni(2) 2.975(2); Ni(1)−CntA 1.763(10); Ni(2)−CntB 1.769(11); P(1)−C(20) 1.859(8); P(2)−C(30) 1.836(9); P(1)−C(16) 1.849(8); P(2)−C(26) 1.857(8). Selected bond angles (deg): P(2)−Ni(1)−P(1) 77.94(9); P(1)−Ni(2)−P(2) 78.02(9); P(2)−Ni(1)−Ni(2) 46.67(6); P(1)−Ni(1)−Ni(2) 46.49(7); P(1)−Ni(2)−Ni(1) 46.69(7); P(2)−Ni(2)−Ni(1) 46.57(7); C(20)−P(1)−C(16) 103.1(4); C(20)−P(1)−Ni(2) 114.0(4); C(16)−P(1)−Ni(2) 120.2(2); C(20)−P(1)−Ni(1) 115.9 (3); C(16)−P(1)−Ni(1) 117.2(3); Ni(2)−P(1)−Ni(1) 86.82(10); C(30)−P(2)−C(26) 103.1(4); C(30)−P(2)−Ni(1) 113.1(4); C(26)−P(2)−Ni(1) 120.0(3); C(30)−P(2)−Ni(2) 115.2(3); C(26)−P(2)−Ni(2) 118.9(3); Ni(1)−P(2)−Ni(2) 86.76(9).

solid state. Crystal, data collection, and refinement parameters are given in Table 2. Atomic coordinates, equivalent isotropic displacement coefficients, and complete lists of bond lengths and angles are in the supporting information, while selected bond lengths and angles are in the figure caption. In contrast to the planar Ni_2P_2 ring in anti **1a** (torsion angle Ni−P···P(A)−Ni(A) = 180°), the ring in **6b** is now puckered (torsion angle Ni(1)-P(1)···P(2)−Ni(2) = 124°). Consequently, the NiCp fragments are closer together (Ni−Ni distance 3.340(2) Å vs 2.975(2) Å). This ring puckering, which presumably also occurs in **1b** and **4b**, is a distortion of the generic syn isomer structure shown in Chart 1.

The relative energies of syn and anti isomers in **1**, **4**, and **6** are presumably controlled by steric interactions of the phosphido groups with the Cp ligands and with each other. The observation in all cases of both isomers shows that the energy differences are small. The anti geometry favored in **1** and **4**, which avoids placing two bulky Mes groups syn to each other, might also be expected in **6**, which contains sterically more demanding phosphido ligands. In this case, however, it is energetically more favorable to pucker the Ni_2P_2 ring, avoiding phosphido-Cp interactions in the anti isomer. Isomerism in the recently reported[11] amido dimers $[Ni(C_5Me_4R')(\mu\text{-}NHR)]_2$ was also suggested to be controlled by steric effects, but direct comparison with these results is difficult because of the difference in size of the cyclopentadienyl ligands in the two systems.

Conclusion

The P−H bonds in **1** provide both a useful spectroscopic probe and a reactive center which allows simple generation of phosphinidene anions **2**, **3**, and **5**. The solution and solid-state structures of **1**, **4**, and **6**, established by NMR spectroscopy and X-ray crystallography, show the small differences in energy between syn and anti isomers in this system. These observations suggest that the deprotonation of dicationic $[L_nM(\mu\text{-}PHR)]_2^{2+}$ complexes will yield cationic or neutral μ-phosphinidene complexes, and we are currently exploring this possibility.

Experimental Section

General Experimental Details. All manipulations were carried out under a nitrogen atmosphere using either standard Schlenk apparatus or a glovebox. Solvents were distilled from sodium and benzophenone (toluene, THF, ether, petroleum ether) or from CaH_2 (methylene chloride) and stored under nitrogen. NMR spectra were obtained at the following frequencies (MHz): ^{31}P, 121.4; ^{13}C, 75.4; ^{1}H, 299.9. Elemental analyses were done by Schwarzkopf Labs, Woodside, NY, or by QTI, Whitehouse, NJ. Mesitylphosphine was prepared by the literature procedure.[17] Methyl iodide was stored over copper wire in the dark.

***anti*-[NiCp(*μ*-PHMes)]$_2$ (1a).** To a slurry of nickelocene (600 mg, 3.18 mmol) in 10 mL of petroleum ether was added PH_2Mes (705 mg, 4.64 mmol). The dark green solution was allowed to stand overnight. The resulting dark brown solution was decanted from a mass of shiny brown-black crystals, which were washed with three 1-mL portions of petroleum ether and dried in vacuo to give 551 mg of the product. A second crop of crystals (90 mg, total yield 641 mg, 73%) was deposited from the mother liquor after 1 more day. Brown crystals suitable for X-ray crystallography were obtained from a saturated THF solution (ca. 50 mg of the compound in 1 mL of THF) at −20 °C. In a similar experiment, the ^{31}P NMR spectrum of the mother liquor was recorded. $^{31}P\{^1H\}$ NMR (petroleum ether, δ): 0.4; −31.1; −36.6; −68.6; −84.4; −153.9; −221.3; −238.5. ^{31}P NMR (petroleum ether, δ): 0.4 (m); −31.1 (d, $J_{PH} = 317$); −36.6 (d, $J_{PH} = 305$); −68.6 (d, $J_{PH} = 211$); −84.4 (d, $J_{PH} = 201$); −153.9 (t, $J_{PH} = 198$, PH_2Mes); −221.3 (m, **1b**); −238.5 (m, **1a**). ^{31}P NMR (CD_2Cl_2, δ): −237.0 (8-line pattern; see Table 1). The spectrum did not change at −40 or 80 °C in toluene-d_8. ^1H NMR (CD_2Cl_2, 21 °C, δ): 6.84−6.75 (broad, 2 overlapping peaks, 4H, Ar); 4.75 (10H, Cp); 3.62 (m, $^2J_{PP} = 432.6$ Hz, $^1J_{PH} = 318.3$ Hz, $^3J_{PH} = -20.5$ Hz, $^4J_{HH} = 5.3$ Hz, 2H, P−H); 3.29 (6H, broad, o-Me); 2.43 (6H, broad, o-Me); 2.24 (6H, p-Me). ^1H NMR (CD_2Cl_2, −20 °C, δ): 6.84 (2H, Ar); 6.73 (2H, Ar); 4.73 (10H, Cp); 3.56 (m, 2H, P−H); 3.27 (6H, o-Me); 2.41 (6H, o-Me); 2.22 (6H, p-Me). ^1H NMR (toluene-d_8, −20 °C, δ): 6.82 (2H, Ar); 6.60 (2H, Ar); 4.77 (10H, Cp); 3.80 (m, 2H, P−H); 3.54 (6H, o-Me); 2.37 (6H, o-Me); 2.11 (6H, p-Me). ^1H NMR (toluene-d_8, 80 °C, δ): 6.71 (4H, Ar); 4.76 (10H, Cp); 3.82 (m, 2H, P−H); 2.87 (very broad, 12H, o-Me); 2.10 (6H, p-Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C, δ): 141.7 (m, ortho Ar); 139.4 (ortho Ar); 136.7 (para Ar); 130.3 (m, ipso Ar); 129.6 (meta Ar); 128.4 (meta Ar); 89.5 (Cp); 23.3 (broad, ortho Me); 20.9 (para Me). IR (KBr): 2915, 2323, 1766, 1711, 1650, 1601, 1549, 1463, 1440, 1404, 1375, 1342, 1290, 1242, 1029, 1011, 984, 945, 871, 846, 830, 780, 683, 615, 576, 551, 458, 410 cm^{-1}. Anal. Calcd for $C_{28}H_{34}Ni_2P_2$: C, 61.15; H, 6.23. Found (Schwarzkopf): C, 61.30; H, 6.39.

syn-[NiCp(*μ*-PHMes)]$_2$ (1b). On standing in solution or, more quickly, on warming, complex **1a** isomerizes to **1b**, which was observed by NMR as an ∼1:5 mixture with **1a**. ^{31}P NMR (CD_2Cl_2, δ): −220.2 (8-line pattern). ^1H NMR (CD_2Cl_2, 21 °C, δ): 4.73 (10H, Cp); 4.20 (4-line pattern; $^2J_{PP} = 364.9$ Hz, $^1J_{PH} = 326.8$ Hz, $^3J_{PH} = -9.4$ Hz, $^4J_{HH} = 3.0$ Hz; 2H, PH).

[NiCp(*μ*-PDMes)]$_2$ (1D) was prepared as for **1a** using PD_2-Mes, which was prepared from PCl_2Mes and $LiAlD_4$.[2e] NMR

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[17] Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Sigel, G. A. *Inorg. Chem.* **1987**, *26*, 1941−1946.

analysis showed the labeled phosphine was about 80% PD$_2$-Mes, 15% PHDMes, and 5% PH$_2$Mes. IR (KBr): 2916, 2325, 1765, 1688, 1650, 1601, 1556, 1454, 1404, 1378, 1342, 1290, 1028, 1010, 984, 881, 868, 846, 836, 778, 660, 614, 560, 523 cm^{-1}. ^{2}H NMR (toluene, δ): 3.84 (broad 3-line pattern, "J" = 22 Hz). This spectrum was simulated using the results for **1a** and the gyromagnetic ratios of ^{1}H and ^{2}H, to give $^2J_{PP}$ = 432.6, $^1J_{PD}$ = 48.9, $^3J_{PD}$ = −3.1,and $^4J_{DD}$ = 0.8 Hz. ^{31}P NMR (toluene, δ): −240.8 (5-line pattern, "J" = 22 Hz). After 1 d in solution the minor isomer **1b** was also observed: δ −223.7 (m).

Deprotonation of 1. Generation of [(NiCp)$_2$(μ-PHMes)(μ-PMes)]$^-$ (2). (a) Li Counterion. To a brown solution of **1** (25 mg, 0.046 mmol) in 1 mL of THF was added *n*-BuLi (50 μL of a 1.6 M solution in hexanes, 0.08 mmol). The solution became darker brown. After 1 h, ^{31}P NMR showed that **2** had formed.

(b) Na Counterion. To a brown solution of **1** (25 mg, 0.046 mmol) and 18-crown-6 (12 mg, 0.045 mmol) in 1 mL of THF was added an excess (10 mg, 0.43 mmol) of freshly cut sodium metal. The solution became darker brown. After 3.5 h, the solution was decanted, and ^{31}P NMR showed that **2** had formed.

Deprotonation of 1D. Generation of [(NiCp)$_2$(μ-PDMes)(μ-PMes)]$^-$ (2D) and Its Methylation To Form 4D. A sample of **1D** (30 mg, 0.054 mmol) in THF (1 mL) was treated with BuLi (50 μL of a 1.6 M solution in hexanes, 0.08 mmol). The solution became darker brown, and ^{31}P NMR after 1 h showed an ~4:1 mixture of **2D** and **2**. ^{31}P{^{1}H} NMR data for **2D** (THF, δ): − 96.1 (d, $^2J_{PP}$ = 198 Hz); −153.4 (dt, $^2J_{PP}$ = 198, $^1J_{PD}$ = 45.8 Hz). After the sample was left standing overnight, some scrambling occurred, and the ratio of **2D** to **2** was ~4:5. Methyl iodide (50 μL, 0.8 mmol) was added directly to the tube containing this mixture, and the ^{31}P NMR spectrum showed that the desired mixture of **4D** and **4**, as a mixture of isomers, had formed. ^{31}P{^{1}H} NMR data for **4D** (THF, δ): −155.6 (d, $^2J_{PP}$ = 375 Hz, minor isomer **b**); −170.3 (d, $^2J_{PP}$ = 429 Hz, major isomer **a**); −215.7 (dt, $^2J_{PP}$ = 375, $^1J_{PD}$ = 48.9, **b**); −227.1 (dt, $^2J_{PP}$ = 429, $^1J_{PD}$ = 48.4, **a**).

Deprotonation of 1. Generation of [NiCp(μ-PMes)]$_2$$^{2-}$ (3). To a brown solution of **1** (30 mg, 0.055 mmol) and 12-crown-4 (30 mg, 0.17 mmol) in 1 mL of THF was added *n*-BuLi (400 μL of a 1.6 M hexanes solution, 0.64 mmol). The solution became darker brown/purple. After 45 min, ^{31}P NMR showed a mixture of monoanion **2** and dianion **3** in ~3:7 ratio. After the tube was stored overnight, only dianion **3** was observed by ^{31}P NMR.

(NiCp)$_2$(μ-PHMes)(μ-PMeMes) (4). To a solution of **1a** (158 mg, 0.288 mmol) in 15 mL of THF was added *n*-BuLi (270 μL of a 1.6 M solution in hexanes, 0.43 mmol). The solution became darker brown immediately. After 1 h, the solution was cooled to −78 °C, and a solution of MeI (270 μL, 4.34 mmol) in THF (5 mL) was added all at once with stirring. The solution was stirred at −78 °C for 15 min and then allowed to warm to room temperature while the solvent and excess MeI were removed in vacuo. The brown residue was extracted with five 5-mL portions of petroleum ether. After filtration through Celite, the solvent was removed from the brown extract, yielding 114 mg of brown crystalline solid (70%). Recrystallization from petroleum ether at −20 °C gives small brown crystals.

This complex exists in solution as an ~4:1 mixture of anti and syn isomers **4a**,**b**. Peaks assigned to minor isomer **4b** are labeled with an asterisk. ^{1}H NMR (toluene-d_8, 22 °C, δ): 6.69; 6.66 (Mes, **4a**,**b**); 4.75 (10H, Cp, **4a**,**b**); 4.16 (dd, $^1J_{PH}$ = 314, $|^3J_{PH}|$ = 17 Hz, 1H, P−H); 3.04 (6H, ortho Me); 3.00 (6H, ortho Me*); 2.82 (6H, ortho Me*); 2.42 (dd, $^2J_{PH}$ = 10.2, $^4J_{PH}$ = 2 Hz, 3H, P−Me*); 2.35 (d, $^1J_{PH}$ = 10.8, 3 H, P−Me); 2.09 (para Me, **4a**,**b**, overlaps solvent peak). ^{1}H NMR (toluene-d_8, − 60 °C, δ): 6.76 (1H, Mes); 6.65; 6.61 (**4a**,**b**), 6.54 (1H, Mes); 4.74 (broad, 10H, Cp, **4a**,**b**); 4.16 (dd, $^1J_{PH}$ = 314, $|^3J_{PH}|$ = 17 Hz, 1H, P−H); 3.32 (3H, ortho Me); 3.05 (6H, ortho Me); 2.98 (6H, ortho Me*); 2.83 (6H, ortho Me*); 2.43 (3H, ortho Me); 2.38 (d, $^2J_{PH}$ = 9 Hz, 3H, P−Me*); 2.27 (d, $^2J_{PH}$ = 9 Hz, 3H, P−Me); 2.05 (para Me, **4a**,**b**, overlaps solvent peak). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C, δ): 141.3; 141.0 (d, J = 7.2); 137.4 (m); 137.1 (m); 135.4 (d, J = 4); 134.2; 131.6 (d, J = 10.5); 130.8 (d, J = 7.2, meta Mes); 130.6 (d, J = 6.6, meta Mes); 129.9 (d, J = 6.6); 90.5 (Cp*); 90.3 (Cp); 26.5 (m); 26.0; 25.9; 25.8; 24.2; 24.1; 24.0; 23.9; 23.2; 23.1; 21.4 (para Me); 21.1 (para Me). IR (KBr): 2958, 2910, 2725, 2303, 1762, 1624, 1601 (s), 1544, 1452(s), 1403, 1374, 1343, 1286, 1272, 1241, 1148, 1098, 1012, 985, 944 cm^{-1}. Anal. Calcd for C$_{29}$H$_{36}$Ni$_2$P$_2$: C, 61.75; H, 6.44. Found (QTI): C, 60.15; H, 6.23. Several attempts gave analytical results low in carbon.

Deprotonation of 4. Generation of [(NiCp)$_2$(μ-PMeMes)(μ-PMes)]$^-$ (5). (a) Li Counterion. Butyllithium (15 μL of a 1.6 M hexane solution, 0.024 mmol) was added to a brown solution of **4** (10 mg, 0.017 mmol) in 1 mL of THF. After 30 min, ^{31}P NMR of the reaction mixture showed that **5** had formed.

(b) Na Counterion. A mixture of **4** (85 mg, 0.15 mmol), 18-crown-6 (45 mg, 0.17 mmol), and excess sodium metal in 10 mL of THF was allowed to stand overnight. The resulting brown solution was decanted from the sodium, and ^{31}P NMR showed that **5** had formed.

Reaction of [NiCp(μ-PMes)]$_2$$^{2-}$ (3) with MeI. Complex **3** was prepared by the addition of BuLi (400 μL of a 1.6 M hexane solution, 0.64 mmol) to a solution of **1a** (30 mg, 0.055 mmol) and 12-crown-4 (30 mg, 0.17 mmol) in THF (5 mL). After 20 h the dark brown solution was cooled to −20 °C and added dropwise with stirring to a similarly cooled solution of MeI (60 μL, 0.96 mmol) in THF (5 mL). The volatile materials were immediately removed in vacuo. The brown residue was extracted with five 2-mL portions of petroleum ether and filtered through Celite. The ^{31}P{^{1}H} NMR spectrum of this brown extract showed the presence of **6a/b**, **4a/b**, and several other unidentified compounds. Adding MeI to a solution of **3** did not improve the yield or the selectivity of the alkylation. Alkylation at −78 °C was also unsuccessful, even when a large excess of MeI was used.

***syn*-[NiCp(μ-PMeMes)]$_2$ (6b).** To a solution of complexes **4a/b** (100 mg, 0.177 mmol) in THF (20 mL) was added BuLi (160 μL of 1.6 M hexane solution, 0.256 mmol). After 6 h, the solution was cooled to −78 °C and MeI (160 μL, 2.57 mmol) in 5 mL of THF was added all at once. The solution was stirred at −78 °C for 15 min and then allowed to warm to room temperature while the solvent and excess MeI were removed in vacuo. The brown residue was extracted with six 5-mL portions of petroleum ether. After filtration through Celite, the solvent was removed from the brown extract, yielding 63 mg of brown solid (62%). This compound is difficult to crystallize, and brown impurity-containing oils are often obtained by this procedure. However, brown needles suitable for X-ray crystallography were grown from petroleum ether at −20 °C. Both crystallography and the analytical data show these are a pentane hemisolvate.

^{1}H NMR (C$_6$D$_6$, δ): 6.43 (4H, Mes); 5.14 (10H, Cp); 2.88 (12H, ortho Me); 2.03 (6H; para Me); 1.01 (t, "J" = 6 Hz, 6H, P−Me). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 143.0 (m, ortho Mes); 137.6 (para Mes); 129.1 (m, Mes); 128.4 (m, obscured by C$_6$D$_6$ peaks, Mes); 92.1 (Cp); 34.8 (para Me); 30.6 (ortho Me); 25.3 (apparent triplet, "J" = 5.5, P−Me). IR (KBr): 2919, 2849, 1734, 1602, 1452, 1263, 1028, 881, 835, 774, 697 cm^{-1}. Anal. Calcd for C$_{30}$H$_{38}$Ni$_2$P$_2$·0.5C$_5$H$_{12}$: C, 63.56; H, 7.24. Found (QTI): C, 63.57; H, 6.97.

Crystal Structure Determinations for 1a and 6b·0.5C$_5$H$_{12}$. Crystal, data collection, and refinement parameters are given in Table 2. The systematic absences in the diffraction data are consistent with *Cc* and *C*2/*c* for **6b**·0.5C$_5$H$_{12}$ and uniquely consistent with *P*2$_1$/*c* for **1a**. The centrosymmetric space group chosen for **6b**·0.5C$_5$H$_{12}$ yielded chemically reasonable and computationally stable results. No absorption corrections were required because of the <10% variation in the ψ-scan integrated intensities. The structures were solved using direct methods and refined by full-matrix least-squares procedures. The molecule in **1a** is located on an inversion center. A half-molecule of pentane solvate was located on a 2-fold axis in **6b**·$0.5C_5H_{12}$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atom bonded to the phosphorus atom in **1a** was located. All other hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in either the SHELXTL (5.3) or the SHELXTL PLUS (4.2) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

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Supporting Information Available: Details of the X-ray structure determinations for **1a** and **6b**, including tables of anisotropic displacement coefficients, complete atom coordinates and isotropic displacement coefficients, and complete bond lengths and angles (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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