# ORGANOMETALLICS

# Cyclopentadiene Alkylation and Nickel Complexes with Tri-, Tetra-, or Pentaisopropylcyclopentadienide or an Even Bulkier Lithium Alkylcyclopentadienide

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**Supporting Information** 

**ABSTRACT:** Phase transfer catalysis has been adapted to the synthesis of triisopropylcyclopentadiene isomers 1 in high yield and purity. Alkylation of sodium triisopropylcyclopentadienides with isopropyl bromide in tetrahydrofuran has been shown to be the currently most efficient way to generate tetraisopropylcyclopentadiene isomers 2, which give sodium tetraisopropylcyclopentadienide (3) upon metalation. The crucial step for the introduction of the fifth isopropyl group, the selective attack of an iminium salt at the tetraisopropylcyclopentadienide anion in the 5-position with generation of the corresponding 1,2,3,4-tetraisopropyl(6-dimethylamino)fulvene (4), has been carried out according to a published procedure. Addition of 1-naphthyllithium to the dimethylaminofulvene 4 yielded extremely bulky lithium dimethylamino-(1-naphthyl)methyltetraisopropylcyclopentadienide (7). Pure 1,2,4,1',2',4'-hexaiso-



propylnickelocene (8) was obtained from sodium triisopropylcyclopentadienide and nickel(II) bromide. The tetraisopropylcyclopentadienylnickel(II) bromide  $[(C_5^i Pr_4 H)Ni(\mu - Br)]_2$  (9) added triphenylphosphine, trimethylphosphine, trimethyl phosphite, and triisopropylphosphine with formation of the diamagnetic phosphine complexes  $[(C_5^{i}Pr_4H)NiBr(PPh_3)]$ (10),  $\left[\left(\bar{C}_{5}^{i}Pr_{4}H\right)NiBr(PMe_{3})\right]$  (13),  $\left[\left(\bar{C}_{5}^{i}Pr_{4}H\right)NiBr\{P(OMe_{3})\}\right]$  (14), and  $\left[\left(\bar{C}_{5}^{i}Pr_{4}H\right)NiBr(P^{i}Pr_{3})\right]$  (15), respectively. The triphenylphosphine derivative 10 displays a dissociation equilibrium with small amounts of 9 in deuteriobenzene solution and could be converted to the methylnickel(II) derivative  $[(C_5^{i}Pr_4H)NiMe(PPh_3)]$  (11) or to the phenyl complex  $[(C_5^{i}Pr_4H)NiPh(PPh_3)]$ (12), respectively. Substitution reactions of the bromide 9 yielded a dinuclear complex with two bridging 2,6-dimethylphenolate ligands,  $[(C_5^i Pr_4 H)Ni(\mu - 2, 6 - OC_6 Me_2 H_3)]_2$  (16), with potassium 2,6-dimethylphenolate and methylene-bridged dinuclear  $[\{(C_5^{i}Pr_4H)Ni\}_2(\mu$ -CH<sub>2</sub>)] (18) with methylmagnesium chloride and concomitant methane formation. Partial hydrolysis converted the phenolate 16 to the monohydroxy derivative  $[\{(C_5^{i}Pr_4H)Ni\}_2(\mu-2,6-OC_6Me_2H_3)(\mu-OH)]$  (17). Crystal structure analyses have been carried out on complexes 8, 11, 13, 14, 16-18, and 20. Lithium pentaisopropylcyclopentadienide (6) reacted with nickel(II) bromide dimethoxyethane adduct in pentane to form the bromo-bridged  $[(C_5^{i}Pr_5)Ni(\mu-Br)]_2$  (19), and the new bulky dimethylamino(naphthyl)methyl-carrying cyclopentadienide 7 reacted with the dimethoxyethane adduct of nickel(II) bromide in pentane to give the diamagnetic alkylcyclopentadienylnickel bromide monomer  $[\{C_5^{i}Pr_4CH(NMe_2)(1-naphthyl)\}NiBr]$  (20). The crystal structure of 20 shows no sign of electron donation from the dimethylamino nitrogen lone pair to the nickel center. The paramagnetism of 19 is in line with similar findings for the pentamethylcyclopentadienyl, tetraisopropylcyclopentadienyl, and 1,2,4tri-tert-butylcyclopentadienyl analogues of 19. The diamagnetism of 20 is most probably due to an empty  $d_z^2$  orbital, which is high in energy because of the combined electron donation from the five-membered ring and the bromo ligand on the z axis.

## INTRODUCTION

Pentaisopropylcyclopentadienyl chemistry started with the synthesis of sodium pentaisopropylcyclopentadienide by a sequence of cyclopentadiene metalation and alkylation reactions<sup>2</sup> and with the elegant synthesis of decaisopropylrhodocenium and pentaisopropyl-cobaltocenium hexafluorophosphate by Astruc.<sup>3</sup> Metallocenes with this bulky pentaalkylcyclopentadienyl ligand are known with calcium, strontium, barium,<sup>4</sup> tin,<sup>5</sup> lead,<sup>6</sup> samarium, europium, ytterbium,<sup>7</sup> and rhodium;<sup>3</sup> half-sandwich complexes with iron have shown interesting reactivity<sup>8</sup> and magnetic properties.<sup>89</sup> The time-consuming cyclopentadiene alkylation process prompted us to reevaluate different approaches toward the introduction of the isopropyl groups.

### SYNTHESIS OF ISOPROPYLCYCLOPENTADIENES

Ammonia as a solvent for cyclopentadiene alkylation has an old tradition,<sup>10</sup> because the titration of the dark blue solution of sodium in ammonia with freshly cracked cyclopentadiene readily provides for fast production of large amounts of sodium cyclopentadienide from solutions of sodium in liquid ammonia. The subsequent nucleophilic substitution of the cyclopentadienide nide anion with isopropyl bromide is straightforward. Another metalation–alkylation sequence can directly follow using

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sodium amide and isopropyl bromide. If large amounts of diisopropylcyclopentadiene are desired, this is the method of choice in our opinion. After distillation diisopropylcyclopentadiene is converted to a mixture of triisopropylcyclopentadiene isomers 1 the same way.<sup>11</sup> The fourth alkylation step can be carried out conveniently in tetrahydrofuran solvent with sodium amide for the metalation and isopropyl bromide as an alkylating agent. While the sodium triisopropylcyclopentadienide isomers are smoothly alkylated to tetraisopropylcyclopentadiene isomers 2 in high yield, a problem shows up, which is geminal dialkylation with generation of the unwanted 5,5diisopropyl isomers 2a,b. These isomers obviously originate from the 1,2,4-triisopropylcyclopentadienide isomer. The geminal dialkylated isomers 2f,g, which could be expected to be formed by geminal dialkylation of the 1,2,3-triisopropylcyclopentadienide, have never been observed in our laboratory. Details are shown in Scheme 1.





Geminal dialkylation converts 40-50% of the triisopropylcyclopentadienide isomeric mixture to cyclopentadienes, which cannot be metalated to cyclopentadienyl anions. This is even worse for the introduction of the fifth isopropyl substituent (Scheme 2). Direct alkylation of sodium tetraisopropylcyclo-

#### Scheme 2. Pentaisopropylcyclopentadiene Isomers by Alkylation of Tetraisopropylcyclopentadienide with Isopropyl Bromide





tadienide more than doubles the yield of the desired 1,2,3,4,5isomer to 11%, which is still unsatisfactory.

A closer look at the alternative process of cyclopentadiene alkylation under phase transfer conditions will show us why a traditional metalation—alkylation procedure is the better way to generate tetraisopropylcyclopentadienes **2** from triisopropylcyclopentadienes **1**.

A one-pot reaction converting cyclopentadiene to tetraisopropylcyclopentadiene is the phase transfer process developed by Dehmlow and Bollmann.<sup>12</sup> With dibenzo-18-crown-6 as a phase transfer catalyst, cyclopentadiene is multiply metalated and alkylated by potassium hydroxide and isopropyl bromide in tetrahydrofuran, resulting in a mixture of tetraisopropylcyclopentadiene isomers **2**. The 70% yield of **2** boils down to a 13.3% yield of sodium tetraisopropylcyclopentadienide, however, because 81% of the isomeric mixture consists of unwanted 5,5-diisopropylated species. The mass of dibenzo-18-crown-6 catalyst needed for the phase transfer process is about equal to the yield of potassium tetraisopropylcyclopentadienide obtained after metalation with potassium hydride. This procedure offers the fastest and most convenient access to small quantities of tetraisopropylcyclopentadienide (Scheme 3).

Scheme 3. One-Pot Phase Transfer Process of Dehmlow and Bollmann, Recommended for Quick and Easy Preparation of Small Amounts of Tetraisopropylcyclopentadiene from Cyclopentadiene



Another phase transfer process was introduced in 1989 by Venier and Casserly<sup>13</sup> and adapted to isopropylcyclopentadienes by Hanusa.<sup>14</sup> Stirring of concentrated aqueous solutions of potassium hydroxide with cyclopentadiene and an excess of isopropyl bromide in the presence of methyltrioctylammonium chloride as a phase transfer catalyst results in multiple cyclopentadiene alkylation. The 1991 publication of Hanusa outlines a separation procedure where mixtures of potassium triisopropylcyclopentadienide and tetraisopropylcyclopentadienide as well as different mixtures of tri- and tetraisopropylcyclopentadienes have to be separated by fractional crystallization (Scheme 4). Hanusa reported a 19% yield of tetraisopropylcy-

Scheme 4. Synthesis of Tetraisopropylcyclopentadiene As Described by Hanusa<sup>13</sup>



clopentadienide, which could be increased to 23% by recycling of mother liquors.<sup>14</sup>

In comparison to the 35% overall yield of sodium tetraisopropylcyclopentadienide obtained by stepwise alkylation,<sup>11,15</sup> the low yield of tetraisopropylcyclopentadienide obtained by this phase transfer procedure may be due to production of large amounts of the unwanted 5,5-diisopropylcyclopentadienes **2a,b**. Although phase transfer obviously is not well suited for the fourth alkylation step, it may still be a time-saving approach for the synthesis of triisopropylcyclopentadienes. We therefore modified the procedure in a search for conditions avoiding the formation of tetraisopropylcyclopentadienes.

Instead of addition of 5 equiv of isopropyl bromide all at once, the reaction was started with addition of 2.5 equiv of isopropyl bromide to the reaction mixture of potassium hydroxide solution, methyltrialkyl( $C_8-C_{10}$ ) ammonium chloride, and cyclopentadiene. The remaining 2.5 equiv of isopropyl bromide was added dropwise, and an almost quantitative yield of triisopropylcyclopentadiene isomers was obtained (Scheme 5).

Scheme 5. Selective Synthesis of Triisopropylcyclopentadienes by Modified Phase Transfer Catalytic Cyclopentadiene Alkylation, Followed by Conversion to Tetraisopropylcyclopentadienide



Column chromatography was omitted; distillation gave a clean mixture of triisopropylcyclopentadiene isomers. A subsequent metalation—alkylation procedure in tetrahydrofuran furnished tetraisopropylcyclopentadiene isomers 2 in 88% yield containing only traces of triisopropylcyclopentadiene. The isomeric mixture consisted of about 50% of the desired isomers 2c-e. Metalation of the oily liquid with sodium amide in tetrahydrofuran gave sodium tetraisopropylcyclopentadienide (3), which was isolated by evaporation of solvent from the filtered solution and washed with petroleum ether in order to remove the 5,5-dialkylation products. The overall yield of sodium tetraisopropylcyclopentadienide from cyclopentadiene was 42%.

The choice of the procedure for tetraisopropylcyclopentadiene synthesis depends on the desired amount of product. For small amounts the procedure of Dehmlow<sup>12</sup> is the most convenient. If larger amounts are needed, the modified phase transfer catalyzed cyclopentadiene alkylation permits the synthesis of 75 g amounts of triisopropylcyclopentadienes from 0.4 mol of cyclopentadiene in a 2 L flask, which is then converted to about half that weight of sodium tetraisopropylcyclopentadienide. Even larger amounts are accessible in one run by sequential alkylation in liquid ammonia. Here, 4 mol of sodium cyclopentadienide can be generated in 2 L of liquid ammonia and converted to about 350 g of sodium tetraisopropylcyclopentadienide in four alkylation–metalation steps.<sup>11,15</sup>

On a search for selective bond formation at the 5-position of tetraisopropylcyclopentadienide, different approaches known from the literature in order to find a reaction capable of regioselective attack at the tetraisopropylcyclopentadienide ion, despite its steric hindrance, were explored. This search finally arrived at a three-step procedure based on the synthesis of 6-dimethylaminopentafulvene reported by Hafner.<sup>16–18</sup> In the first step tetraisopropylcyclopentadienide is attacked selectively at the 5-position by the dimethylaminomethoxycarbenium ion generated by alkylation of dimethylformamide with dimethyl sulfate. 1,2,3,4-Tetraisopropyl-6-dimethylaminofulvene (4) is obtained as a crystalline solid, which contains varying amounts of tetraisopropylcyclopentadiene and requires purification by crystallization or sublimation (Scheme 6).





In the second step methyllithium is added, followed by chlorodimethylsilane. By spontaneous dimethylaminodimethylsilane elimination the fulvene skeleton is regenerated and 1,2,3,4-tetraisopropyl-6-methylfulvene **5** is formed, which can be converted to the lithium pentaisopropylcyclopentadienide diethyl ether adduct **6** by addition of methyllithium in diethyl ether.<sup>1</sup>

The dimethylaminofulvene **4** has now been found to be capable of 1-naphthyllithium addition despite its steric bulk (Scheme 7).

Scheme 7. Formation of 7 by Addition of 1-Naphthyllithium to the Dimethylaminofulvene 4



The pale yellow salt is quite soluble in all common organic solvents, including pentane, and stable at room temperature as a solid or in solution under inert gas. Upon heating decomposition was observed at temperatures exceeding 60 °C. The <sup>13</sup>C NMR spectrum of 7 displays a characteristic high-field signal at 2.3 ppm, which has been assigned to a localized carbanion. This localization is probably a consequence of lithium coordination to the nitrogen donor in the dimethylamino side chain.

Scheme 8. Formation of Hexaisopropylnickelocenes from Nickel(II) Bromide and a Mixture of Sodium Triisopropylcyclopentadienide Isomers



# NICKEL COMPLEXES

The contrast between the melting point of 1,1',2,2',4,4'hexaisopropylferrocene (172 °C<sup>11</sup>) and the value of 107-110 °C mentioned for 1,1',2,2',4,4'-hexaisopropylnickelocene (8) in a chapter on melting points of metallocenes within a review article<sup>19</sup> drew our attention to this nickelocene derivative.<sup>20</sup> The nickelocene was formed in a smooth reaction from nickel(II) bromide dimethoxyethane adduct and a solution of the two sodium triisopropylcyclopentadienide isomers (1,2,4and 1,2,3-isomers in an approximate 4:1 ratio) (Scheme 8). The color observed during sodium triisopropylcyclopentadienide addition was dark brown in the beginning, which is probably due to a mono(triisopropylcyclopentadienyl) complex and the color of the metallocene, which mixed in as a green component while the second equivalent of the sodium salt was added. The workup was not optimized for high yield, but crystallization of the product was carried out in order to obtain the pure main isomer  $[(1,2,4-iPr_3C_5H_2)_2Ni]$  (8), while leaving the two other possible isomers  $[(1,2,3-iPr_3C_5H_2)_2Ni]$  and  $[(1,2,4-iPr_3C_5H_2)(1,2,3-iPr_3C_5H_2)Ni]$  in the mother liquor. The crude product obtained from the petroleum ether extract melted at 117 °C; triple recrystallization gave samples with melting points of 146, 151, and 151 °C. Because proton NMR spectra of the paramagnetic compound exhibit broad signals and do not permit the detection of traces of impurities, we cannot rule out a small contamination with isomers containing residual 1,2,3triisopropylcyclopentadienide in our sample, however.

X-ray crystal structure investigation of a green single crystal of 8 (Figure 1; details regarding the crystal structure analyses are given in Table 1) showed a centrosymmetric molecule like that of other hexaisopropyl metallocenes<sup>21-23</sup> or the



Figure 1. ORTEP drawing of the 1,2,4,1',2',4'-hexaisopropylnickelocene 8. Distances (Å) and angles (deg): Ni1–C1 = 2.1912(16), Ni1–C2 = 2.1910(16), Ni1–C3 = 2.1909(17), Ni1–C4 = 2.2104(16), Ni1–C5 = 2.1867(16), Ni–Cp<sub>cent</sub> = 1.827, Ni–C(av) = 2.190, C1– C2 = 1.428(2), C2–C3 = 1.431(2), C3–C4 = 1.422(2), C4–C5 = 1.426(2), C5–C1 = 1.432(2); Cp<sub>cent</sub>–Ni–Cp<sub>cent</sub> = 180.

parent nickelocene.<sup>24</sup> The rings are planar and the isopropyl groups do not create much strain, because the isopropyl group at the 4-position with its two hydrogen neighbors is able to turn its methyl groups outside and stretch one methyne hydrogen toward the other ring, where it finds ample space between the two adjacent isopropyl groups rotated away from each other.

The two adjacent isopropyl groups of the other ring are rotated apart from each other in order to leave as much space as possible for the 4-isopropyl substituent. The same conformation has been found for all crystal structures of metallocenes with this substituent pattern known so far. The metal–ring centroid distance of 1.827 Å is slightly longer than the value of 1.794 Å found for the parent nickelocene.<sup>24</sup>

The triphenylphosphine complex  $[(C_5^{i}Pr_4H)NiBr(PPh_3)]$ (10) can be synthesized in a one-pot reaction from nickel(II) bromide dimethoxyethane adduct by introduction of sodium tetraisopropylcyclopentadienide 3, followed by addition of triphenylphosphine (Scheme 9). The red-violet needles can be handled in air without visible change and are thermally stable and sparingly soluble in petroleum ether.

Solutions of 10 are air-sensitive, however, and deuteriobenzene solutions of analytically pure 10 always exhibit the broad low-field NMR signals of very small amounts of the paramagnetic, phosphine-free nickel bromide dimer  $[(C_5^{i}Pr_4H)Ni(\mu Br)]_2$  (9) in addition to the signals of diamagnetic 10. These observations can be explained assuming a dissociation equilibrium, which is shifted strongly toward the diamagnetic phosphine complex:

$$2[(C_5^{i}Pr_4H)Ni(PPh_3)(Br)]$$

$$10$$

$$\approx [(C_5^{i}Pr_4H)Ni(\mu-Br)]_2 + 2PPh_3$$
9

A small fraction of complex 10 dissociates in deuteriobenzene solution.

With methylmagnesium chloride **10** forms the corresponding methyl complex  $[(C_5^{i}Pr_4H)NiCH_3(PPh_3)]$  **11**, whose solubility in petroleum ether is slightly better than that of **10**. Proton NMR spectra of **11** exhibit a doublet at -0.62 ppm with  ${}^{3}J_{P,H} = 6.9$  Hz for the methyl group bound to the nickel center. The spectra show no signs of phosphine dissociation, which may be understood as a consequence of the slightly released steric bulk compared to the bromo complex **10**. Phosphine dissociation could still occur below the detection limit of NMR spectroscopy.

The green complex could be crystallized from toluene solution as monoclinic blocks. The X-ray crystal structure analysis (Figure 2) reveals a half-sandwich complex with a Ni– $Cp_{cent}$  distance of 1.77 Å, which is shorter than the Ni– $Cp_{cent}$  distance of 1.794 Å in the parent nickelocene.<sup>24</sup> The alkylcyclopentadienyl ring plane of **11** is oriented almost perpendicular to the plane defined by the nickel atom and its two  $\sigma$ -bonded ligand atoms (phosphorus and methyl carbon).

Table 1. Details Regarding	the Crystal Struc	ture Analyses of (	Complexes 11, 13,	14, 16–18, and 20				
	8	11	13	14	16	17	18	20
formula	$C_{28}H_{46}N_i$	$\rm C_{36}H_{47}NiP$	C <sub>20</sub> H <sub>38</sub> BrNiP	$\rm C_{20}H_{38}BrNiO_{3}P$	$C_{50}H_{76}Ni_2O_2$	$\mathrm{C_{42}H_{67}Ni_2O_2}$	C <sub>35</sub> H <sub>60</sub> Ni <sub>2</sub>	$\rm C_{30}H_{42}BrNNi$
formula wt	220.68	569.42	448.09	496.09	826.53	721.38	598.25	555.27
cryst size (mm)	$0.70 \times 0.25 \times 0.12$	$0.58 \times 0.40 \times 0.14$	$0.46 \times 0.30 \times 0.20$	$0.58 \times 0.28 \times 0.22$	$0.43 \times 0.42 \times 0.39$	$0.48 \times 0.32 \times 0.12$	$0.48 \times 0.32 \times 0.12$	$0.11 \times 0.10 \times 0.04$
space group	PĪ	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1$	$\overline{PI}$	$P2_1/c$	Cc
lattice params								
a (Å)	8.753(1)	9.6646(6)	15.061(4)	17.719(4)	10.4040(8)	10.0100(9)	12.2297(19)	17.5710(6)
b (Å)	9.081(1)	23.3369(19)	8.6453(12)	8.270(8)	14.2093(8)	12.6008(11)	15.732(2)	17.2638(8)
c (Å)	9.260(1)	14.4152(9)	18.079(3)	33.570(8)	15.6601(12)	17.1516(15)	17.792(2)	37.9120(25)
$\alpha$ (deg)	79.75(1)	06	90	06	06	74.631810)	06	90
$\beta$ (deg)	80.04(1)	92.818(7)	93.36(3)	93.364(5)	93.878(9)	87.691(10)	97.957(6)	100.440(5)
$\gamma$ (deg)	61.76(1)	06	60	06	06	76.631(10)	60	90
V (Å <sup>3</sup> )	634.73(12)	3247.3(4)	2349.8(8)	4919(5)	2309.8(3)	2029.0(3)	3390.2(8)	11309.9(10)
Ζ	2	4	4	8	2	2	4	16
$T(\mathbf{K})$	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(1)	150(2)
$D_{ m calcd}$ (g cm <sup>-3</sup> )	1.155	1.165	1.267	1.340	1.188	1.181	1.172	1.304
$\mu \ (\mathrm{cm}^{-1})$	7.75	6.68	25.93	24.93	8.51	9.59	11.30	27.53
transmissn factors	0.6129-0.9127	0.59242-0.85156	0.3996-0.5724	0.323- 0.592		0.7302-0.8936		0.640 - 1.000
$\theta$ limits (deg)	2.25-29.99	2.74-27.48	2.72-25.68	2.30-27.50	2.82-26.02	2.61-26.02	1.68 - 22.48	3.62-63.25
total no. of rflns	4451	54 098	32 317	7151	13 311	29 318	6033	55 373
no. of indep rflns	3650	7300	4458	5936	3440	7483	4339	16 507
abs cor	numerical	numerical	empirical (MULABS)	empirical (DELABS)	none	analytical (ABST)	none	semiempirical (multiscan)
structure soln	direct methods	direct methods	direct methods	direct methods	direct methods	direct methods	direct methods	direct methods
program used	SIR92	SHELXS-97	SHELXS-97	SHELXS-97	<b>26-SXIEHS</b>	SIR92	SHELXS-97	SHELXS-97
refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
no. of data/restraints/params	3650/0/139	7300/0/352	4458/7/229	5936/277/491	3440/0/283	7483/24/443	4339/0/333	16 507/2/1230
R1, wR2 $(I > 2\sigma(I))$	0.0408, 0.0941	0.0326, 0.0783	0.0317, 0.0672	0.0494, 0.0534	0.0464, 0.1090	0.0401, 0.0937	0.0531. 0.1144	0.0529, 0.1278
R1, wR2 (all data)	0.0517, 0.0987	0.0513, 0.0833	0.0612, 0.0746	0.2322, 0.0815	0.0747, 0.1179	0.0689, 0.1032	0.0932, 0.1318	0.012, 0.1387
GOF (all data)	1.062	0.960	0.858	0.718	0.914	0.882	1.017	0.945
max/min difference peak (e Å <sup><math>-3</math></sup> )	0.420, -0.534	0.292, -0.344	0.266, -0.307	0.362,0.421	0.268, -0.291	0.551, -0.389	0.417, -0.503	1.936, -0.561

Scheme 9. Synthesis of Phosphine Complexes 10-15 from the Bromo-Bridged Dimer 9



**Figure 2.** ORTEP drawing of the methylnickel complex **11**. Distances (Å) and angles (deg): Ni–C = 1.9936(19), Ni–C1 = 2.2020(16), Ni–C2 = 2.1574(17), Ni–C3 = 2.1071(16), Ni–C4 = 2.1681(16), Ni–C5 = 2.1116(15), Ni-Cp<sub>cent</sub> = 1.770, C1–C2 = 1.410(2), C2–C3 = 1.471(3), C3–C4 = 1.426(2), C4–C5 = 1.430(2), C5–C1 = 1.432(2); C6–Ni–P = 89.19(7); dihedral angle between the Cp ring plane and the plane defined by Ni, P, and C6  $90.2^{\circ}$ .

The phosphine ligand is located underneath the only ring hydrogen substituent for steric reasons. The two isopropyl groups on C2 and C3 are rotated away from each other in order to provide as much space as possible for the methyl ligand underneath. The nickel-methyl carbon distance of 1.9936(19) Å is comparable to the values found for tetragonal-planar nickel(II) diphosphine thiophenolate complexes of the type  $[(R_2PC_2H_4PR_2)NiCH_3(S-Ar')]$  with Ni–CH<sub>3</sub> distances between 1.96 and 1.99 Å, where the aryl group Ar' is a phenyl or pentafluorophenyl group (three examples) or carries a side chain with an NH group forming a hydrogen bridge to the thiolate sulfur atom (five examples).<sup>25</sup> Also comparable is a pentamethylcyclopentadienyl analogue of 11 with a triethylphosphine ligand,  $[(C_5Me_5)NiCH_3(PEt_3)]^{.26}$  In this complex a Ni–C distance of 1.96(1) Å was observed, but the structure could not be well refined because of a crystallographic pseudo mirror plane. Two independent molecules of the benzyl derivative  $[(C_5Me_5) NiCH_{2}Ph(PEt_{3})$ ] described in the same publication show Ni-Cdistances of 1.979(3) and 2.007(4) Å, and the Ni-CH<sub>3</sub> distance in the diphosphine nickel(II) complex  $[({}^{i}Pr_{2}C_{2}H_{4}P^{i}Pr_{2})-$ NiCH<sub>3</sub>(CHMePh)] was found to be 1.987(4) Å.<sup>2</sup>

The phenylnickel complex  $[(C_5^{i}Pr_4H)NiC_6H_5(PPh_3)]$  (12) was obtained in 43% yield as a greenish powder from the bromide starting complex and phenylmagnesium bromide and is easily soluble in petroleum ether, diethyl ether, and toluene. In addition to the proton NMR signals of the tetraisopropylcyclopentadienyl ligand with their 1:2:2:6:6:6:6 integral ratio a multiplet between 6.8 and 7.5 ppm corresponds to 20 protons for three phenyl rings attached to phosphorus and one to nickel. The signals of the phenyl group bound to the nickel atom could not be distinguished from those of the phosphine phenyl signals. Here, as in the case of the methyl complex 11, phosphine dissociation has not been observed by NMR spectroscopy.

Upon addition of 2 equiv of trimethylphosphine or trimethyl phosphite the bromo complex  $[(C_5^{i}Pr_4H)Ni(\mu-Br)]_2$  was converted to the red trimethylphosphine complex  $[(C_5^{i}Pr_4H) NiBr(PMe_3)$  (13) or to the orange-brown trimethyl phosphite complex  $[(C_5^{i}Pr_4H)NiBr{P(OMe)_3}]$  (14), respectively. The methyl substituents of the trimethylphosphine ligand of 13 are split into doublets with about the same coupling constant as the methyl protons of the isopropyl groups, but shifted to lower field by about 0.5 ppm. Prominent signals in the EI mass spectrum of 13 are those of the molecular ion (44.5%), the tetraisopropylcyclopentadienyl cation (32%), the trimethylphosphinyl radical cation (83.5%), the dimethylphosphenium cation (100%), and the isopropyl cation (70%); smaller signals are fragmentation products of the tetraisopropylcyclopentadienyl ligand. The methoxy proton signal of 14 is a doublet with a  ${}^{3}J_{P,H}$  coupling constant of 11.8 Hz

Complexes 13 (Figure 3) and 14 (Figure 4) show conformations very similar to that of the triphenylphosphine



**Figure 3.** ORTEP drawing of the trimethylphosphine complex **13**. Distances (Å) and angles (deg): Ni–Br = 2.331(2)/2.324(3), Ni–P = 2.1556(9), Ni–C1 = 2.164(3), Ni–C2 = 2.167(3), Ni–C3 = 2.152(3), Ni–C4 = 2.148(3), Ni–C5 = 2.018(3), Ni–C $_{\text{cent}}$  = 1.749, C1–C2 = 1.396(4), C2–C3 = 1.485(4), C3–C4 = 1.406(4), C4–C5 = 1.434(4), C5–C1 = 1.435(4); Br–Ni–P = 92.69(13)/90.8(2); dihedral angle between the Cp ring plane and the plane defined by Ni, P, and Br1  $91.8^{\circ}$ . The bromo ligand is disordered. The disorder was refined to the Br1 position with 60% probability and the Br2 position with 40% probability. Ellipsoids are at the 50% probability level.

derivative **11** with a methyl ligand. In all three cases the phosphine is located underneath the only ring proton and the bromo or methyl ligand sits between two isopropyl groups of the cyclopentadienyl ligand, which are rotated away from each other. Structural details for comparison are compiled in Table 2.



Figure 4. ORTEP drawing of the trimethylphosphite complex 14. Distances (Å) and angles (deg): Ni–Br = 2.336(3)/2.333(3), Ni–P = 2.095(5)/2.115(5), Ni–C1 = 2.168(15)/2.202(15), Ni–C2 = 2.180(17)/2.118(15), Ni–C3 = 2.152(17)/2.155(16), Ni–C4 = 2.112(15)/2.149(15), Ni–C5 = 2.062(13)/ = 2.009(14), Ni-C<sub>pent</sub> = 1.762/1.754, C1–C2 = 1.370(19)/1.41(2), C2–C3 = 1.47(2)/1.51(2), C3–C4 = 1.37(2)/1.340(19), C4–C5 = 1.442(18)/1.421(18), C5–C1 = 1.440(16)/1.396(17); Br–Ni–P = 94.43(17)/94.71(18); dihedral angle between the Cp ring plane and the plane defined by Ni, P, and Br 91.9/87.4.

Table 2. Structural Details of the Tetraisopropylcyclopentadienylnickel(II) Phosphine Complexes  $[(C_5^{i}Pr_4H)NiCH_3(PPh_3)]$  (11),  $[(C_5^{i}Pr_4H)NiBr(PMe_3)]$  (13), and  $[(C_5^{i}Pr_4H)NiBr{P(OMe)_3}]$  (14)

	11	13 <sup><i>a</i></sup>	$14^b$
Ni-Cp <sub>cent</sub>	1.770	1.746	1.762 (A)
			1.754 (B)
Ni-Br		2.331(2)	2.336(3) (A)
		2.324(3)	2.333(3) (B)
Ni-P	2.1256(5)	2.1556(9)	2.095(5) (A)
			2.115(5) (B)
Ni-CH <sub>3</sub>	1.9936(19)		
Ni–C(av) Cp ring	2.1492	2.1298	2.135 (A)
			2.127 (B)
dihedral angle <sup>c</sup>	90.2	91.8 (Br1)	91.9 (A)
		84.1 (Br2)	87.4 (B)
			h_

<sup>*a*</sup>Disorder of the bromo ligand, positions Br1 and Br2. <sup>*b*</sup>Two independent molecules A and B. <sup>*c*</sup>Dihedral angle between the cyclopentadienyl plane and the plane containing nickel, phosphorus, and the second  $\sigma$ -bonded ligand (bromide or methyl carbon atom).

The violet crystals of the triisopropylphosphine complex  $[(C_5^{i}Pr_4H)NiBr(P^iPr_3)]$  (15) are easily soluble in pentane and other organic solvents. The solutions are very air-sensitive and change from violet to brown and green upon contact with air. The broadened proton and phosphorus NMR signals of 15 as well as the signals of small amounts of the bromo-bridged dimer 9 in the proton NMR spectrum of 15 indicate phosphine dissociation similar to the triphenylphosphine derivative 10, but more pronounced.

The bromo complex 9 has also been used for substitution reactions with anionic nucleophiles.

A red-brown tetrahydrofuran solution of **9** slowly turned orange-brown upon stirring with potassium 2,6-dimethylphenolate (Scheme 10). The orange, solid product  $[(C_5^{i}Pr_4H)Ni(\mu-2,6-OC_6Me_2H_3)]_2$  (**16**) is soluble in pentane and other organic Scheme 10. Synthesis of the 2,6-Dimethylphenolate Complex 16 and Its Partial Hydrolysis Product 17



solvents and very air-sensitive both as a solid or in solution. Proton NMR spectra are typical for a paramagnetic complex with broad or very broad signals between 37 and -16 ppm and halfwidths from 15 to 300 Hz. According to the Eyring equation,<sup>28</sup> the large chemical shifts provide for high signal coalescence temperatures and enable the observation of rotamers at room temperature. As a consequence, there are many broad signals of varying intensity at high and low field belonging to different rotamers, which makes the interpretation of spectra difficult. An exemplary NMR investigation of three paramagnetic alkylcyclopentadienylnickel bromides will be devoted to this problem.<sup>31</sup> The EI mass spectrum of the 2,6-dimethylphenolate 16 did not show a molecular ion but instead the monomeric  $[(C_5^{i}Pr_4H)]$ -Ni $(OC_6Me_2H_3)$ ]<sup>+</sup> cation with m/z 412 and 92% intensity in addition to a parent peak for an oxidation product of the composition  $[(C_5^{i}Pr_4H)Ni(OC_6Me_2H_3)_2NiO]^+$  and a small signal for  $[(C_5^{i}Pr_4H)Ni(OC_6Me_2H_3)_2]^+$ . 16 did not crystallize readily from solution. After several manipulations and solvent changes finally a few orange crystals could be obtained by slow evaporation of a mixture of pentane and cyclopentene, which are most probably a result of partial hydrolysis of 16 in solution. 16 could be crystallized, however, by vacuum sublimation in a sealed glass tube at 60 °C over a couple of weeks. The partial hydrolysis product  $[(C_5^{1}Pr_4H)Ni(\mu-2,6-OC_6Me_2H_3)(\mu-OH)Ni (C_5^{i}Pr_4H)$ ] (17) was characterized by an X-ray crystal structure analysis only.

The Ni…Ni distances of both dinuclear phenolate complexes (3.134(2) and 3.099(2) Å, respectively; Figures 5 and 6) are clearly nonbonding, and the Cp<sub>cent</sub>-Ni distances are very similar to those of the nickelocene 8 but longer than those observed for the diamagnetic phosphine complexes 11, 13, and 14 (see Table 2), for the methylene-bridged dinickel complex 18 (1.753/1.752 Å for Ni1 and Ni2, respectively), and for the monomeric bromide 20 (1.729, 1.729, 1.751, and 1.757 Å for four independent molecules A-D.

Solid methylmagnesium chloride diethyl etherate causes a solution of the bromo-bridged dimer **9** to turn black. Bubbles indicating concomitant gas evolution may be seen, if the Grignard compound is added quickly. The black powder obtained from the reaction mixture is easily soluble in pentane and other organic solvents. In addition to the signals expected for the tetraisopropylcyclopentadienyl ligand, the <sup>13</sup>C NMR spectrum shows a triplet at 65.9 ppm with <sup>1</sup> $J_{C,H} = 145$  Hz. Proton NMR spectra show a singlet at 3.64 ppm with the same intensity as that of the tetraisopropylcyclopentadienyl ring proton. The hypothesis of a dinickel complex with a methylene bridge [{( $C_5^{i}Pr_4H$ )Ni}\_2( $\mu$ -CH<sub>2</sub>)] (18) could be confirmed by a crystal structure analysis.



**Figure 5.** Crystal structure of the bis(2,6-dimethylphenolate) complex **16.** Distances (Å) and angles (deg): Ni1-··Ni1A = 3.134(2), Ni1-O1 = 1.981(2), Ni1-O2 = 1.986(2), Ni1-C1 = 2.207(4), Ni1-C2 = 2.210(3), Ni1-C3 = 2.230(3), Ni1-C4 = 2.179(3), Ni1-C5 = 2.161(4), Ni1-Cp<sub>cent</sub> = 1.828, C1-C2 = 1.447(5), C2-C3 = 1.448(5), C3-C4 = 1.430(5), C4-C5 = 1.413(6), C5-C1 = 1.425(6); Ni1-O1-Ni1A = 104.52(16), Ni1-O2-Ni1A = 104.20(15), O1-Ni1-O1A = 75.42(11); dihedral angle between two five-membered-ring planes 180 by symmetry, dihedral angle between both aryl planes and the Cp plane 7.2, dihedral angle between the planes defined by Ni1, Ni1A, O1 and Ni1, Ni1A, O2 8.0.



Figure 6. Crystal structure of the partial hydrolysis product 17. Distances (Å) and angles (deg): Ni1…Ni2 = 3.099(2), Ni1–O1 = 1.9824(19), Ni2– O1 = 1.986(2), Ni1-O2 = 1.925(11), Ni1-O3 = 1.948(4), Ni2-O2 =1.902(11), Ni2-O3 = 1.948(5), Ni1-C1 = 2.200(3), Ni1-C2 = 2.184(3), Ni1-C3 = 2.211(3), Ni1-C4 = 2.189(3), Ni1-C5 = 2.161(3), Ni2-C6 = 2.178(3), Ni2-C7 = 2.174(3), Ni2-C8 = 2.207(3), Ni2-C9 = 2.198(3), Ni2-C10 = 2.171(3), Ni1-Cp<sub>cent</sub> = 1.820, Ni2–Cp<sub>cent</sub> = 1.824, C1–C2 = 1.428(4), C2–C3 = 1.447(4), C3–  $C4 = 1.429(\bar{4}), C4-C5 = 1.428(4), C5-C1 = 1.420(4), C6-C7 =$ 1.468(5), C7-C8 = 1.438(5), C8-C9 = 1.401(4), C9-C10 = 1.373(5),C6-C10 = 1.390(5); Ni1-O1-Ni2 = 102.72(9), Ni1-O2-Ni2 =108.2(6), Ni1-O3-Ni2 = 105.4(3), O1-Ni1-O2 = 72.9(5), O1-Ni1-O3 = 75.45(14), O1-Ni2-O2 = 73.3(5), O1-Ni2-O3 = 75.36(14);dihedral angle between two five-membered-ring planes 8.7°, dihedral angle between aryl plane and Cp plane (C1-C5) 3.5, dihedral angle between aryl plane and Cp plane (C6-C10) 5.2.

The Ni–Cp<sub>cent</sub> distances of 1.753 and 1.752 Å for Ni1 and Ni2, respectively, are shorter than in the phenolate-bridged dinuclear complexes and compare well with the valued found for the diamagnetic phosphine complexes (see Table 2). The Ni–CH<sub>2</sub> distances between 1.87 and 1.89 Å as well as the Ni–Ni distance of 2.316 Å are quite short (Figure 7). In accordance



**Figure 7.** Crystal structure of the methylene complex **18.** Distances (Å) and angles (deg): Ni1–Ni2 = 2.3158(10), Ni1–C18 = 1.869(12), Ni1–C18A = 1.886(14), Ni2–C18 = 1.892(11), Ni2–C18A = 1.869(13), Ni1–C1 = 2.138(5), Ni1–C2 = 2.138(5), Ni1–C3 = 2.109(5), Ni1–C4 = 2.131(5), Ni1–C5 = 2.138(5), Ni2–C21 = 2.131(5), Ni2–C22 = 2.117(5), Ni2–C23 = 2.127(5), Ni2–C24 = 2.130(5), Ni2–C25 = 2.144(5); C18–Ni1–C18A = 30.3(5), Ni1–C18–Ni2 = 76.0(4), Ni1–C18A–Ni2 = 76.1(5), C18–Ni1–Ni2 = 52.4(3), C18–Ni2–Ni1 = 51.5(4), C18A–Ni1–Ni2 = 51.5(4), C18A–Ni1–Ni2 = 51.5(4), C18A–Ni1–Ni2 = 51.5(4). The methylene bridge is disordered and was refined assuming an equal distribution over both positions C18 and C18A. Attempted refinement of an occupation parameter for these positions did not improve the quality of the structure solution.

with these observations, the 15-valence-electron CpNi fragments call for a Ni=Ni double bond and two Ni-C single bonds.

The formation of the dinuclear complex 18 obviously involves  $\alpha$ -hydride abstraction, which could produce a mononuclear methylene complex with 18 valence electrons as has been postulated by Pasynkiewicz.<sup>28</sup> The hypothetical, highly reactive intermediate  $[({}^{i}Pr_{4}C_{5}H)NiH(CH_{2})]$  could be in an equilibrium with the 16-valence-electron species  $[({}^{i}Pr_{4}C_{5}H)-$ NiCH<sub>3</sub>] and the tetrahydrofuran adduct thereof (Scheme 11). Two such molecules are necessary for the formation of one molecule of complex 18 together with 1 equiv of methane as a plausible byproduct. A very similar hypothesis has been put forward by Pasynkiewicz et al.<sup>30</sup> for the reaction of nickelocene with methyllithium in the presence of 2-hexene, where the olefin takes the role of the additional donor ligand. The dinuclear complex  $[CpNi(\mu-CH_2)NiCp]$  was postulated as an intermediate, but analogues of 18 with less bulky cyclopentadienyl ligands could not be detected or isolated before, which is probably due to follow-up reactions with formation of higher nuclearity complexes (cf. ref 30).

Since the diethyl ether adduct of lithium pentaisopropylcyclopentadienide is soluble in pentane, its reaction with the dimethoxyethane adduct of nickel(II) bromide was carried out in pentane solution at ambient temperature and proceeded smoothly within a few hours (Scheme 12). The product **19** was obtained in 69% yield as a crystalline solid, which is soluble in pentane and very soluble in other organic solvents such as Scheme 11. Hypothesis on the Formation of the Dinuclear Methylene Complex 18



toluene, diethyl ether, tetrahydrofuran, and methylene chloride. 19 is very sensitive toward air or moisture but can be stored under inert gas at room temperature and even sublimed at 70 °C and  $10^{-2}$  mbar and decomposes upon heating above 80 °C. Combustion analysis results are in accord with the expected pentaisopropylcyclopentadienylnickel(II) bromide.

Proton NMR spectra in deuteriobenzene show three broad signals with an intensity ratio of 3:3:1. Two signals of equal intensity at 38.3 and 34.5 ppm with a half-width of 195 Hz originate from the methyl protons and can be attributed to five methyl groups oriented outward and five methyl groups close to the nickel center. The smaller resonance of the isopropyl methyne protons was found at 18.6 ppm with a half width of 250 Hz. A discussion of NMR spectra and dynamic properties of the <sup>5</sup>Cp ligand has been published.<sup>4</sup> The paramagnetism of  $[(C_5H^iPr_4)Ni(\mu-Br)]_2$  (19), the tetraisopropylcyclopentadienyl analogue of 8, has been investigated by magnetic susceptibility measurements in the solid state and by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy in solution at variable temperature.<sup>31</sup> The dimeric structure of 9 in the solid state was determined by X-ray crystallography and mentioned in refs 20, 32, and 33. From these findings and their parallels we infer that the paramagnetic pentaisopropylcyclopentadienylnickel bromide 19 is a dimer with bromo bridges according to the formula  $[(C_5^{i}Pr_5)Ni(\mu$ Br)]<sub>2</sub> (Scheme 12) and possesses two unpaired electrons at each nickel center, although it must be viewed as an 18 valence electron complex. Possible reasons for this behavior will be discussed after the introduction of complex 20, which is an example of the contrary.

Lithium tetraisopropyldimethylamino(naphthyl)methylcyclopentadienide (7) and the dimethoxyethane adduct of nickel bromide in pentane also gave an intense red solution, from which the intense red nickel complex 20 could be isolated (Scheme 13). The crystalline compound was heated at  $10^{-2}$ mbar and decomposed above 85 °C without noticeable

Scheme 12. Reaction of the Pentane-Soluble Lithium Pentaisopropylcyclopentadienide Diethyl Ether Adduct with Nickel(II) Bromide Dimethoxyethane Complex To Form the Dimeric Bromide  $[{}^{5}CpNi(\mu-Br)]_{2}$  (19)



sublimation. 20 can be stored at room temperature under inert gas but decomposes quickly upon contact with air.

<sup>1</sup>H NMR spectra of **20** show two sets of sharp and wellresolved signals within a spectral window between 0.9 and 7.9 ppm. 20 is diamagnetic and seems to consist of two diastereomers. Each isopropyl methyl group of each diastereomer has its own doublet with  ${}^{3}J_{H,H}$  coupling constants between 6.35 and 7.56 Hz, which gives 16 doublets between 0.4 and 1.56 ppm. The full data set can be found in the Experimental Procedures. <sup>13</sup>C NMR spectra exhibit 20 signals, which have been assigned to the naphthyl moieties of 2 species with very similar spectra and interpreted as the signals of 2 diastereomers.

The reason for diastereomer formation has to be the addition of the naphthyl substituent to the former =CH(NMe<sub>2</sub>) group with formation of a center of chirality. Since the five interlocking substituents at the five-membered ring are too sterically hindered for rotation, the combination of a chirality center at one substituent and axial chirality caused by the directionality of the isopropyl and the dimethylamino-(naphthyl)methyl substituent around the five-membered ring creates two diastereomers visible in the NMR spectra, with each diastereomer consisting of two enantiomers.

Slow evaporation of a pentane solution of 20 gave crystals suitable for X-ray diffraction. The unit cell belongs to the space group Cc and contains four independent molecules. All of them are monomeric half-sandwich complexes and carry the nickel bromide fragment in the vicinity of the dimethylamino group. The diastereomers with nickel in the vicinity of the naphthyl group must be present in solution but do not show up in the crystal picked for X-ray diffraction. The ring-nickel distance

Scheme 13. Reaction of the Pentane-Soluble Lithium Dimethylamino(1-naphthyl)methyltetraisopropylcyclopentadienide Diethyl Ether Complex with Nickel(II) Bromide Dimethoxyethane Complex To Form the Monomeric Complex  $[{R_4C_5CH(1-C_{10}H_7)(NMe_2)}NiBr]$  (20)



varies between 1.729 and 1.757 Å, and the angle between the Ni–Br bonds and the Cp ring planes varies between 5.9 and 7.0°. The terminal nickel–bromine distance is shorter than the Ni–Br distances in the bromo-bridged dimer 9 (average 2.425 Å) and even shorter than in the phosphine complexes 13 and 14 (average 2.330 Å; for details see Table 2). More data are given along with Figure 8.



**Figure 8.** ORTEP drawing of the nickel complex **20**. Distances (Å) and angles (deg): Ni1–C1 = 2.083(10), Ni1–C2 = 2.141(8), Ni1–C3 = 2.122(9), Ni1–C4 = 2.142(7), Ni1–C5 = 2.124(7), Ni1–Cp<sub>cent.</sub> = 1.729, Ni1–Br1 = 2.2483(19), Ni2–C9 = 2.094(10), Ni2–C19 = 2.118(8), Ni2–C29 = 2.126(8), Ni2–C39 = 2.114(9), Ni2–C49 = 2.141(8), Ni2–C102 = 2.131(7), Ni3–C103 = 2.122(11), Ni3–C101 = 2.178(11), Ni3–C102 = 2.131(7), Ni3–C103 = 2.122(11), Ni3–C104 = 2.124(8), Ni3–C105 = 2.128(8), Ni3–Cp<sub>cent</sub> = 1.751, Ni3–Br3 = 2.242(2), Ni4–C109 = 2.182(11), Ni4–C119 = 2.152(7), Ni4–C129 = 2.139(8), Ni4–C139 = 2.105(9), Ni4–C149 = 2.116(8), Ni4–Cp<sub>cent</sub> = 1.757, Ni4–Br4 = 2.236(2); dihedral angles between Cp ring planes and the Ni–Br vectors within each of the four independent molecules Ni1–Br1 84.1, Ni2–Br2 83.5, Ni3–Br3 83.4, Ni4–Br4 83.0.

With respect to the steric bulk in the proximity of the metal atom this five-membered ring is the bulkiest cyclopentadienyl ligand known to us. The dimethylamino group extends far into the narrow space on the metal side of the ring, so that even a bromo-bridged dimer is unfavorable for steric reasons. Our initial idea of nitrogen lone pair coordination to the nickel center being responsible for monomer formation proved wrong. Not only is the lone pair not pointing toward the nickel atom but also the small displacement of the bromo ligand out of the axial position tells us that nitrogen coordination is not a valid assumption in this case. The dimethylamino group seems to act as a steric obstacle in the proximity of the central atom and is bulky enough to hinder dimer formation.

The bromo-bridged dimer **19** is thought to be monomeric in the gas phase, because a sublimation temperature of 70  $^{\circ}$ C at a pressure of 0.01 mbar is very low for a complex with more than 1400 atomic mass units.

The paramagnetism of **19** was noted in ref 33. A diamagnetic ground state is expected for nickel(II) with a  $d^8$  configuration, if the two d orbitals highest in energy are separated by a gap exceeding the spin pairing energy. The coordination number at nickel in complexes **9** or **19** is 5, the coordination geometry is not very symmetric, and there is no pair of ligands exerting their electron-repelling influence on the same nickel d orbital.

Furthermore, the ligands do not provide a strong ligand field. For these reasons the splitting between the two d orbitals highest in energy is too small to enforce a diamagnetic ground state for complexes 9 and 19.

The monomeric half-sandwich complex **20** happens to be diamagnetic. In this case there must be one d orbital significantly higher in energy than the second highest one in order to make spin pairing attractive. This could be the  $d_{z^2}$  orbital, whose energy is increased not only by the pentaalkylcyclopentadienyl ligand on one side but also by the only bromo ligand on the other side.

There are, of course, many diamagnetic nickel(II) complexes with 16 valence electrons, which are planar. The geometry of complex **20** resembles more a distorted tetrahedron, where diamagnetic species of this type are rare. One example for a geometrically similar and diamagnetic nickel(II) complex with a distorted-tetrahedral ligand sphere is the bromo derivative of a nickel(II) complex with a bulky tris(3,5-diphenyl)pyrazolylborate ligand.<sup>34</sup>

#### CONCLUSION AND OUTLOOK

Several routes for tetraisopropylcyclopentadienide and a quite efficient three-step procedure for lithium pentaisopropylcyclopentadienide from tetraisopropylcyclopentadienide pave the way toward transition-metal complexes of sterically demanding alkylcyclopentadienyl ligands and facilitate the synthesis of dinuclear mono(alkylcyclopentadienyl) complexes. The paramagnetism of cyclopentadienylnickel complexes with 18 valence electrons is not as well established as that of nickelocenes with 20 valence electrons. The dinuclear nickel complex 16 with 2,6dimethylphenolate bridges and the bromo-bridged dimer 19 not only exhibit broad NMR signals in a wide spectral window but also their nickel(II)–Cp<sub>cent</sub> distances are markedly longer than those found for the diamagnetic 18-valence-electron nickel(II) phosphine complexes 11, 13, and 14, the methylene-bridged dinuclear complex 18, and the mononuclear 16-valence-electron cyclopentadienylnickel(II) bromide 20. While these observations can be explained by the stronger ligand field exerted by phosphines or the methylene bridge as compared to that of  $\pi$ donor ligands such as phenolate or bromide, the difference between the dinuclear bromide 19 and the mononuclear bromide 20 is more subtle and is presumably due to the geometry of the complex. The almost linear Br-Ni-Cp<sub>cent</sub> arrangement provides for a relatively strong combined ligand influence on the  $d_{z^2}$  orbital despite the weak ligand field of only one bromo ligand in addition to the five-membered ring.

The methylene-bridged complex **18** is an example of a species never before encountered with less bulky cyclopentadienyl ligands and supports the postulation of a  $C_5H_5$  analogue of **18** as an unstable intermediate during reactions of nickelocene with methyllithium.<sup>30</sup>

The observation of the facile sublimation of bis[bromo-(pentaisopropylcyclopentadienyl)nickel] (19) but even more the monomeric structure of complex 20 with an even bulkier alkylcyclopentadienyl ligand suggest that a critical bulk has been achieved, where transition-metal complexes with still lower coordination number can be stabilized as electronically unsaturated monomers, whose reactivity will have to be investigated further.

#### EXPERIMENTAL PROCEDURES

Synthetic work has been carried out under inert gas in rigorously dried and deoxygenated solvents using Schlenk line techniques for the

preparation of fulvenes and alkali-metal cyclopentadienide salts and an argon-filled glovebox from MBraun, Garching, Germany, for preparation and handling of the nickel complexes. Solvents have been dried under inert gas with molten alkali metals such as potassium (tetrahydrofuran) or sodium/potassium alloy (diethyl ether, petroleum ether, pentane) and distilled prior to use. NMR spectra were obtained on Bruker DPX 400 and Avance 600 NMR spectrometers and referenced to the residual solvent signals: chemical shifts  $\delta$  are given in ppm and coupling constants J in Hz. Elemental analyses have been carried out in the analytical laboratory of the chemistry department of the TU Kaiserslautern. Gas chromatograms have been taken on a Shimadzu GC-17A with flame ionization detector equipped with a column of 30 m length, 0.32 mm inner diameter, and a poly(5% diphenyl/95% dimethylsiloxane) layer of 0.25  $\mu$ m thickness. The injector temperature and the column temperature in the beginning was 70 °C and was increased by 50 °C/min to a limit of 280 °C; the detector temperature was 280 °C. The synthesis of lithium pentaisopropylcyclopentadienide followed the protocol developed by Dezember in our research group.

Triisopropylcyclopentadiene Isomers 1. A 2 L four-necked round-bottom flask equipped with a mechanical stirrer, dropping funnel, reflux condenser, thermometer, and heating mantle was charged with potassium hydroxide solution (50%, 1 L solution made from 750 g of potassium hydroxide and 750 mL of water), methyltrialkyl $(C_8 - C_{10})$ ammonium chloride (Adogen 464, 13.5 g), and freshly cracked cyclopentadiene (32 mL, 0.4 mol). The mixture was stirred vigorously, while 2-bromopropane was admitted within 2 min (90 mL, 117.9 g, 0.96 mol). Another portion of 2-bromopropane (98 mL, 128.4 g, 1.04 mol) was added dropwise within 1 h. The inner temperature went up to 52-55 °C and was raised to 65 °C within 3-4 h and kept for another 9 h. Stirring was maintained throughout this procedure. The mixture was cooled to ambient temperature, and the phases were separated. A solid precipitate of potassium bromide was discarded. The aqueous phase was extracted with petroleum ether (ca. 150 mL) and set aside for a second run after addition of potassium hydroxide (112 g, 2 mol). From the combined organic extracts petroleum ether was removed by rotary evaporation. The remaining oil was distilled in vacuo without prior use of drying agents, because the water comes out together with a small forerun (ca. 5 mL) consisting of diisopropylcyclopentadiene with traces of triisopropylcyclopentadiene. The pale yellow main fraction was collected in a boiling range of 75-95 °C at a pressure of 6 mbar and found to contain triisopropylcyclopentadiene isomers 1 and only traces of di- and tetraisopropylcyclopentadiene and amounted to a yield of 75 g (0.389 mol, 97%).

GC data: several peaks between 5.9 and 6.4 min retention time.

Tetraisopropylcyclopentadiene Isomers 2. To a stirred mixture of sodium amide (15.1 g, 0.4 mol) and tetrahydrofuran (300 mL) in a 1 L three-necked round-bottom flask equipped with a mechanical stirrer, dropping funnel, reflux condenser, and heating mantle were added triisopropylcyclopentadiene isomers (76.2 g, 0.4 mol) and the suspension was slowly heated to a gentle reflux. After 8 h the evolution of ammonia had ceased and the concentrated, viscous, brown solution of sodium triisopropylcyclopentadienide isomers was cooled to 40 °C. Upon dropwise addition of 2-bromopropane (48.7 g, 0.4 mol) the temperature rose again and a colorless solid precipitated from the solution. Gradually the brown color faded away and the viscosity was gradually reduced. After heating to reflux for 1 h, stirring was continued while the mixture was cooled to ambient temperature. Cautious addition of water (15 mL) and removal of most of the solvent by distillation left a mixture, which was extracted with diethyl ether (200 mL). From the extract the product was isolated by solvent evaporation and distillation, yielding a main fraction of tetraisopropylcyclopentadiene isomers (81.3 g, 0.346 mol, 88%) in a boiling range of 70-85 °C at a pressure of 0.1 mbar.

GC data: several peaks between 7.8 and 8.3 min retention time.

**Sodium Tetraisopropylcyclopentadienide (3).** A suspension of sodium amide (16 g, 0.41 mol) in a solution of tetraisopropylcyclopentadiene isomers (70 g, 0.30 mol) in tetrahydrofuran (350 mL) was heated to reflux for 60 h. During this time the slow evolution of ammonia was observed and the solution turned brown. When the gas evolution had ceased, the solution was filtered through a medium-porosity glass frit and the solvent was removed from the filtrate in vacuo. The residual sludge was treated with petroleum ether (250 mL) and filtered through a medium-porosity glass frit. The solid product was washed thoroughly with petroleum ether, dried in vacuo, and stored under inert gas. The yield was 38.6 g (0.15 mol, 50%) of ivory powder.

GC data: a small sample was hydrolyzed with a mixture of diethyl ether and water and gave two signals at 7.9 and 8.0 min.

Lithium Tetraisopropyl-5-{(dimethylamino)(naphth-1-yl)methyl]cyclopentadienide (7). A solution of 1-naphthyllithium (926 mg, 6.91 mmol) in diethyl ether (20 mL) was added dropwise to a solution of tetraisopropyl-6-dimethylaminofulvene (2.00 g, 6.91 mmol) in diethyl ether (20 mL) cooled in an ice bath. The ice bath was thawed to ambient temperature, and stirring was continued for 48 h. During this period the color of the solution changed from intense red to pale orange. Evaporation of the solution, stirring of the residue with pentane, and fractional crystallization of the product from pentane solution yielded the pure product in moderate yield (1.58 g, 3.7 mmol, 54%). Anal. Calcd for C<sub>30</sub>H<sub>42</sub>LiN: C, 85.06; H, 9.99. Found: C, 84.93; H, 9.21. <sup>1</sup>H NMR (600 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ 7.65-7.85 (br, 7H, naphthyl), 7.35-7.55 (br, 7H, naphthyl), 3.61 (sep, 1H,  ${}^{3}J_{\rm H,H} = 7.33$ ), 3.42 (sep, 1H,  ${}^{3}J_{\rm H,H} = 7.33$ ), 3.22 (sep, 1H,  ${}^{3}J_{\rm H,H} = 6.35$ ), 2.74 (sep, 1H,  ${}^{3}J_{H,H}$  = 7.33), 2.25 (s, 1H, CHNMe<sub>2</sub>C<sub>10</sub>H<sub>7</sub>), 1.62 (d, 3H,  ${}^{3}J_{H,H} = 7.33$ , CH(CH<sub>3</sub>)<sub>2</sub>), 1.50 (d, 6H,  ${}^{3}J_{H,H} = 7.33$ , CH(CH<sub>3</sub>)<sub>2</sub>), 1.40 (d, 6H,  ${}^{3}J_{\text{H,H}}$  = 7.33, CH(CH<sub>3</sub>)<sub>2</sub>), 1.38 (d, 3H,  ${}^{3}J_{\text{H,H}}$  = 7.33, CH(CH<sub>3</sub>)<sub>2</sub>), 1.38 (d, 3H,  ${}^{3}J_{\text{H,H}}$  = 7.33, CH(CH<sub>3</sub>)<sub>2</sub>), 1.3-1.5 (br, 6H, N(CH<sub>3</sub>)<sub>2</sub>), (1.03 (d, 3H,  ${}^{3}J_{\text{H,H}}$  = 6.35, CH(CH<sub>3</sub>)<sub>2</sub>), 0.99 (d, 3H,  ${}^{3}J_{\text{H,H}}$  = 6.35, CH(CH<sub>3</sub>)<sub>2</sub>).  ${}^{13}\text{C}^{\{1\text{H}\}}$  NMR (C<sub>6</sub>D<sub>6</sub>): δ 150.9 (C3 of Cp ring), 147.9 (C2 of Cp ring), 146.9 (C2 of Cp ring), 139.3 (naphthyl), 137.8 (naphthyl), 136.7 (naphthyl), 134.7 (naphthyl), 134.2 (naphthyl), 132.3 (naphthyl), 130.6 (naphthyl), 129.5 (naphthyl), 129.3 (naphthyl), 128.5 (naphthyl), 128.4 (naphthyl), 127.1 (naphthyl), 126.5 (naphthyl), 126.3 (naphthyl), 126.2 (naphthyl), 125.8 (naphthyl), 125.4 (naphthyl), 124.4 (naphthyl), 34.6 (CHMe<sub>2</sub>), 33.4 (isopropyl CH<sub>3</sub>), 33.3 (isopropyl CH<sub>3</sub>), 27.6 (CHMe<sub>2</sub>), 27.5 (CHMe<sub>2</sub>), 27.1 (CHMe<sub>2</sub>), 25.0 (NCH<sub>3</sub>), 24.5 (NCH<sub>3</sub>), 23.3 (isopropyl CH<sub>3</sub>), 22.9 (isopropyl CH<sub>3</sub>), 21.8 (isopropyl CH<sub>3</sub>), 21.0 (isopropyl CH<sub>3</sub>), 14.4 (isopropyl CH<sub>3</sub>), 2.3 (Li-C)

1,1',2,2',4,4'-Hexaisopropylnickelocene (8). A suspension of nickel(II) bromide dimethoxyethane complex (800 mg, 2.59 mmol) in tetrahydrofuran (30 mL) was stirred at -30 °C, and a solution of sodium triisopropylcyclopentadienide isomers consisting of ca. 78% 1,2,4- and 22% 1,2,3-triisopropylcyclopentadienide (1.11 g, 5.18 mmol) was added dropwise. The mixture turned brown immediately and changed to olive green when more than half of the sodium salt solution had been added. The mixture was thawed to ca. 10 °C, and then the solvent was removed in vacuo. The olive green residue was extracted with petroleum ether (60 mL), and the insoluble material was separated by centrifugation. The volume of the organic extract was reduced in vacuo to ca. 10 mL, at which point incipient crystallization was observed. At -40 °C green crystals were obtained within 1 day (200 mg, 0.45 mmol, 17.5%), which showed a melting point of 117 °C. After repeated recrystallization from petroleum ether melting points of 146, 151, and 151 °C could be observed and crystals suitable for X-ray diffraction could be isolated. Anal. Calcd for C<sub>28</sub>H<sub>46</sub>Ni: C, 76.20; H, 10.51. Found: C, 75.50; H, 10.42. <sup>1</sup>H NMR (400 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  (half width) 29.43 ( $\Delta \nu_{1/2}$  = 220 Hz, 6H, CH<sub>3</sub>), 10.91  $(\Delta \nu_{1/2} = 210 \text{ Hz}, 6\text{H}, CH_3), 0.47 (\Delta \nu_{1/2} = 150 \text{ Hz}, 6\text{H}, CH_3).$ 

**Bromo(1,2,3,4-tetraisopropylcyclopentadienyl)**-(triphenylphosphine)nickel(II) (10). To a suspension of nickel(II) bromide dimethoxyethane adduct (7.57 g, 24.5 mmol) in tetrahydrofuran (100 mL) stirred at -20 °C was added a solution of sodium tetraisopropylcyclopentadienide (6.10 g, 23.8 mmol) in tetrahydrofuran (80 mL) via addition funnel within a couple of minutes. The reaction mixture turned dark brown quickly. Solid triphenylphosphine (6.55 g, 25.0 mmol) was added immediately thereafter, and the mixture was stirred for 1 h at that temperature and thawed to +10 °C. After removal of volatiles in vacuo the red residue was extracted with toluene (200 mL) at room temperature. Filtration and removal of the toluene gave a brown-red solid, which was washed with four portions of petroleum ether (20 mL each). The first washings turned brownish; the last portion of petroleum ether had a light, transparent red color. Drying in vacuo yielded red, microcrystalline product **9** (8.80 g, 13.9 mmol, 57.5%), which melted at 212 °C. Anal. Calcd for C<sub>35</sub>H<sub>44</sub>BrNiP: C, 66.40; H, 6.99. Found: C, 66.28; H, 7.00. <sup>1</sup>H NMR (400 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.93 (br, 3H, phenyl *H*), 7.33 (m, 3H, phenyl *H*), 7.15 (m, 9H, phenyl *H*), 3.61 (d, 1H, *J*<sub>P,H</sub> = 3.5 Hz, Cp ring *H*), 3.29 (sep, 2H, *J*<sub>H,H</sub> = 6.9 Hz, CHMe<sub>2</sub>), 2.61 (sep, 2H, *J*<sub>H,H</sub> = 6.9 Hz, CHMe<sub>2</sub>), 1.87 (sep, 6H, *J*<sub>H,H</sub> = 6.9 Hz, CH<sub>3</sub>), 1.28 (d, 6H, *J*<sub>H,H</sub> = 6.9 Hz, CH<sub>3</sub>), 1.02 (d, 6H, *J*<sub>H,H</sub> = 7.0 Hz, CH<sub>3</sub>), 0.91 (d, 6H, *J*<sub>H,H</sub> = 6.9 Hz, CH<sub>3</sub>). <sup>31</sup>P NMR (160 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  32.5 ppm.

Methyl(1,2,3,4-tetraisopropylcyclopentadienyl)-(triphenylphosphine)nickel(II) (11). To a solution of 9 (1.641 g, 2.59 mmol) in diethyl ether (80 mL) was added crystalline methylmagnesium chloride diethyl ether adduct (407 mg, 2.73 mmol) in one portion at room temperature. The red solution turned brown quickly and green after 12 h of stirring. The solvent was evaporated, and the residue was extracted with petroleum ether (50 mL). After centrifugation the deep green solution was concentrated to 20 mL and stored at -85 °C to yield a green, microcrystalline powder (700 mg, 1.30 mmol, 48%), which melted at 172 °C. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a toluene solution of 10. Anal. Calcd for C<sub>36</sub>H<sub>47</sub>NiP: C, 75.93; H, 8.32. Found: C, 74.96; H, 8.05. <sup>1</sup>H NMR (400 MHz, 298 K,  $C_6D_6$ ):  $\delta$  7.68–7.78 (m, 6H, phenyl H), 6.99–7.11 (m, 9H, phenyl H), 4.16 (d, 1H,  $J_{P,H}$  = 2.2 Hz, Cp ring H), 3.25 (sep, 2H,  $J_{H,H}$  = 6.9 Hz, CHMe<sub>2</sub>), 2.54 (sep, 2H,  $J_{H,H}$  = 6.9 Hz, CHMe<sub>2</sub>), 1.66 (sep, 6H,  $J_{H,H}$  = 6.9 Hz, CH<sub>3</sub>), 1.37 (sep, 6H,  $J_{H,H}$  = 6.9 Hz,  $CH_3$ ), 1.18 (sep, 6H,  $J_{H,H}$  = 6.9 Hz,  $CH_3$ ), 1.02 (sep, 6H,  $J_{H,H}$  = 6.9 Hz,  $CH_3$ ), -0.62 (d, 3H,  $J_{P,H}$  = 6.9 Hz, Ni- $CH_3$ ). <sup>31</sup>P NMR (160 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ 48.5 ppm.

Phenyl(1,2,3,4-tetraisopropylcyclopentadienyl)-(triphenylphosphine)nickel(II) (12). To a solution of 9 (0.50 g, 0.79 mmol) in tetrahydrofuran (20 mL) was added a solution of phenylmagnesium bromide diethyl ether adduct (142 mg, 0.55 mmol) at room temperature. The red solution turned dark, and stirring was continued for 12 h. The solvent was evaporated, and the residue was extracted with petroleum ether (40 mL). After centrifugation the olive green solution was evaporated until seed crystals appeared. At -85 °C green, microcrystalline 11 (150 mg, 0.237 mmol, 43%) was obtained, which melted between 107 and 109 °C. Anal. Calcd for C41H49NiP: C 77.97; H, 7.82. Found: C, 76.65; H, 7.54. <sup>1</sup>H NMR (400 MHz, 298 K,  $C_6D_6$ ):  $\delta$  6.82–7.55 (m, 20H, phenyl H), 4.56 (s, 1H, Cp ring H), 2.99  $(\text{sep, 2H, CHMe}_2)$ , 2.83  $(\text{sep, 2H, CHMe}_2)$ , 1.50  $(\text{sep, 6H, } J_{\text{H,H}} = 7.0$ Hz, CH<sub>3</sub>), 1.22 (sep, 6H,  $J_{H,H}$  = 6.6 Hz, CH<sub>3</sub>), 1.13 (sep, 6H,  $J_{H,H}$  = 7.2 Hz,  $CH_3$ ), 1.08 (sep, 6H,  $J_{H,H}$  = 7.3 Hz,  $CH_3$ ). <sup>31</sup>P NMR (160 MHz, 298 K,  $C_6D_6$ ):  $\delta$  42.4 ppm.

Bromo(1,2,3,4-tetraisopropylcyclopentadienyl)-(trimethylphosphine)nickel(II) (13). To a solution of  $bis\{\mu$ bromo(tetraisopropylcyclopentadienyl)nickel} (440 mg, 0.59 mmol) in tetrahydrofuran (15 mL) stirred at -10  $^\circ \check{C}$  was added trimethylphosphine (0.12 mL, 1.18 mmol). A deep red solution was obtained and warmed to room temperature. Stirring was continued for 12 h, and then the solvent was evaporated and the residue was extracted with petroleum ether (20 mL). After centrifugation the orange-brown solution was concentrated until incipient crystallization was observed. At -20 °C orange-red crystals were formed in 310 mg (0.69 mmol, 59%) yield. Mp: 159-161 °C. Anal. Calcd for C<sub>20</sub>H<sub>38</sub>BrNiP: C, 53.61; H, 8.55. Found: C, 53.57; H, 8.74. <sup>1</sup>H NMR (400 MHz, 298 K,  $C_6D_6$ ):  $\delta$  3.56 (d, 1H,  $J_{P,H}$  = 4.8 Hz, ring H), 3.16 (sep, 2H, CHMe<sub>2</sub>), 2.59 (sep, 2H, CHMe<sub>2</sub>), 1.72 (d, 9H,  $J_{P,H}$  = 7.1 Hz, PCH<sub>3</sub>), 1.29 (d, 6H,  $J_{H,H}$  = 7.2 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.20 (d, 6H,  $J_{\rm H,H}$  not observed because of superposition, CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (d, 6H,  $J_{H,H}^{I,H} = 6.7 \text{ Hz}, \text{ CH}(\text{CH}_3)_2), 1.05 \text{ (d, 6H, } J_{H,H} = 6.8 \text{ Hz}, \text{ CH}(\text{CH}_3)_2).$ <sup>31</sup>P NMR (160 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -11.9 (br).

Bromo(1,2,3,4-tetraisopropylcyclopentadienyl)(trimethyl phosphite)nickel(II) (14). To a solution of bis $\{\mu$ -bromo-(tetraisopropylcyclopentadienyl)nickel $\}$  (350 mg, 0.47 mmol) in tetrahydrofuran (15 mL) stirred at room temperature was added

trimethyl phosphite (0.11 mL, 0.94 mmol). The solution turned orange-brown and stirring was continued for 2 h; then the solvent was evaporated and the residue was extracted with petroleum ether (50 mL). After centrifugation the orange-brown solution was concentrated until incipient crystallization was observed. At -20 °C orange-red crystals were formed in 300 mg (0.60 mmol, 64%) yield. Single crystals for X-ray diffraction were grown from petroleum ether solution at -20 °C. Anal. Calcd for C<sub>20</sub>H<sub>38</sub>BrNiO<sub>3</sub>P: C, 48.42; H, 7.72. Found: C, 48.20; H, 7.76. <sup>1</sup>H NMR (400 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.63 (d, 9H,  $J_{P,H} = 11.8$  Hz, OCH<sub>3</sub>), 3.61 (d, 1H,  $J_{P,H} = 2.6$  Hz, ring H), 2.99 (sep, 2H, CHMe<sub>2</sub>), 1.25 (d, 6H,  $J_{H,H} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.23 (d, 6H,  $J_{H,H} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.03 (d, 6H,  $J_{H,H} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P NMR (160 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  35.7 (s).

Bromo(1,2,3,4-tetraisopropylcyclopentadienyl)-(triisopropylphosphine)nickel(II) (15). To a solution of  $bis{\mu$ bromo(tetraisopropylcyclopentadienyl)nickel} (350 mg, 0.47 mmol) in tetrahydrofuran (20 mL) stirred at -15 °C was added triisopropylphosphine (0.18 mL, 0.94 mmol) dropwise. The solution turned reddish within 1 min. The solution was warmed to room temperature, and then the solvent was evaporated and the violet residue was extracted with petroleum ether (50 mL). After centrifugation the violet solution was concentrated until the formation of seed crystals was observed. At -20 °C violet product could be crystallized (284 mg,(0.53 mmol, 57%). Anal. Calcd for C<sub>26</sub>H<sub>50</sub>BrNiP: C, 58.67; H, 9.47. Found: C, 58.57; H, 9.20. <sup>1</sup>H NMR (400 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ 3.90 (br, 1H, ring H), 3.30 (sep, 2H, CHMe<sub>2</sub>), 2.57 (sep, 2H, CHMe<sub>2</sub>), 1.76 (br, 3H, PCHMe<sub>2</sub>), 1.29 (br, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.20 (br, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (br, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.05 (br, 6H,  $CH(CH_3)_2$ ). The broad methyl signals of the isopropyl substituents of the phosphine ligand are partially hidden under the isopropyl signals of the cyclopentadienyl ring. <sup>31</sup>P NMR (160 MHz, 298 K,  $C_6D_6$ ):  $\delta$  44.4 (br)

Bis{(µ-2,6-dimethylphenolato)(1,2,3,4-tetraisopropylcyclopentadienyl)nickel(II)} (16). Solid bis{ $\mu$ -bromo(tetraisopropylcyclopentadienyl)nickel} (340 mg, 0.457 mmol) was mixed with a solution of potassium 2,6-dimethylphenolate (155 mg, 0.967 mmol) in tetrahydrofuran (20 mL) and stirred at room temperature overnight. The solvent was evaporated, and the orange-brown residue was extracted with petroleum ether (30 mL). After centrifugation the volume of the orange extract was reduced to 10 mL by evaporation and the concentrate was stored at -40 °C. The product was obtained as an orange, crystalline solid (273 mg, 0.33 mmol, 72%). The extremely air sensitive solid could not be analyzed, because the compound decomposed during sample manipulation. Crystals for X-ray diffraction have been obtained by vacuum sublimation in a sealed glass tube under vacuum over a couple of weeks at 60 °C. <sup>1</sup>H NMR (400 MHz, 298 K,  $C_6D_6$ ): signals of high intensity,  $\delta$  (half width) 23.65 ( $\Delta \nu_{1/2}$  = 110 Hz), 21.64 ( $\Delta \nu_{1/2}$  = 15 Hz), 16.90  $(\Delta \nu_{1/2} = 240 \text{ Hz})$ , 15.05  $(\Delta \nu_{1/2} = 190 \text{ Hz})$ , 12.80 (superposition), 11.60 (superposition); signals of low intensity,  $\delta$  (half width) 37.06  $(\Delta \nu_{1/2} = 35 \text{ Hz})$ , 36.01  $(\Delta \nu_{1/2} = 300 \text{ Hz})$ , 34.89 (superposition), 33.61 ( $\Delta \nu_{1/2}$  = 15 Hz), 30.47 (superposition), 26.46 ( $\Delta \nu_{1/2}$  = 25 Hz),  $-9.52 (\Delta v_{1/2} = 20 \text{ Hz}), -14.27 (\Delta v_{1/2} = 15 \text{ Hz}), -15.59 (\Delta v_{1/2} =$ 15 Hz).

Crystallization from solution was unsuccessful. Repeated attempts at crystal growth from solutions in different solvents and solvent mixtures finally produced crystals from a mixture of pentane and cyclopentene, which were suitable for X-ray diffraction. These orange crystals consisted of the partial hydrolysis product ( $\mu$ -2,6-dimethylphenolato)-( $\mu$ -hydroxo)bis{(1,2,3,4-tetraisopropylcyclopentadienyl)nickel(II)} (17), which was apparently formed during the crystallization experiments with traces of water.

**Methylenebis**{(1,2,3,4-tetraisopropylcyclopentadienyl)nickel(II)} (18). To a magnetically stirred, red-brown solution of bis{ $\mu$ -bromo(1,2,3,4-tetraisopropylcyclopentadienyl)nickel(II)} (519 mg, 0.697 mmol) in tetrahydrofuran (15 mL) at room temperature was added solid methylmagnesium chloride diethyl ether adduct (220 mg, 1.48 mmol) at once. The solution turned black, and stirring was continued for 14 h. The solvent was evaporated, and the black residue was extracted with petroleum ether (80 mL). After centrifugation the solvent was removed in vacuo and the crude black product was stirred with acetonitrile (3–4 mL). The solution was discarded, and the insoluble product was dried to yield 250 mg (0.418 mmol, 60%) of a black powder. Anal. Calcd for  $C_{35}H_{60}N_{12}$ : C, 70.26; H, 10.10. Found: C, 69.11; H, 9.77. <sup>1</sup>H NMR (400 MHz, 298 K,  $C_6D_6$ ):  $\delta$  4.64 (s, 2H, ring H), 3.64 (br, 2H, CHMe<sub>2</sub>), 3.23 (br, 2H, CHMe<sub>2</sub>), 2.28 (d, 6H,  $J_{\rm H,H}$  = 6.2 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.71 (d, 6H,  $J_{\rm H,H}$  = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.57 (d, 6H,  $J_{\rm H,H}$  = 6.7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.41 (s, 2H, CH<sub>2</sub> bridge), 1.29 (d, 6H,  $J_{\rm H,H}$  = 6.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, 298 K,  $C_6D_6$ ):  $\delta$  72.8 (d, 2C, <sup>1</sup>J<sub>C,H</sub> 171 Hz, ring CH), 65.9 (t, 1C, <sup>1</sup>J<sub>C,H</sub> = 145 Hz, bridging CH<sub>2</sub>), 36.5 (q, 4C, <sup>1</sup>J<sub>C,H</sub> = 125 Hz, CH<sub>3</sub>), 35.6 (q, 4C, <sup>1</sup>J<sub>C,H</sub> = 125 Hz, CH<sub>3</sub>), 32.6 (q, 4C, <sup>1</sup>J<sub>C,H</sub> = 121 Hz, CHMe<sub>2</sub>), 19.4 (d, 4C, <sup>1</sup>J<sub>C,H</sub> = 121 Hz, CHMe<sub>2</sub>). Ring C<sup>1</sup>Pr signals could not be assigned because of a combination of low signal intensity and high noise.

**Bromopentaisopropylcyclopentadienylnickel Dimer 19.** To a stirred suspension of nickel(II) bromide dimethoxyethane adduct (260 mg, 0.84 mmol) in pentane (5 mL) was added a solution of lithium pentaisopropylcyclopentadienide diethyl ether adduct (300 mg, 0.84 mmol) in pentane (15 mL). Over 3 days the stirred mixture changed from a pale salmon to an intense red. Insolubles were settled by centrifugation, stirred up with pentane (10 mL), and subjected to centrifugation again. Upon evaporation to dryness the combined pentane extracts yielded 240 mg (0.58 mmol, 69%) of a dark red, crystalline solid. Anal. Calcd for C<sub>40</sub>H<sub>70</sub>Br<sub>2</sub>Ni<sub>2</sub>: C, 58.01; H, 8.52. Found: C, 57.76; H, 8.48. <sup>1</sup>H NMR (600 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ 38.3 (Δν<sub>1/2</sub> = 195 Hz, 15H, CH<sub>3</sub>), 34.5 (Δν<sub>1/2</sub> = 195 Hz, 15H, CH<sub>3</sub>), 18.6 (Δν<sub>1/2</sub> = 250 Hz, 5H, CH).

Bromotetraisopropyl-5-(dimethylaminonaphth-1-yl)methylcyclopentadienylnickel (20). To a stirred suspension of nickel(II) bromide dimethoxyethane adduct (150 mg, 0.49 mmol) in pentane (20 mL) was added a solution of lithium tetraisopropyl-5dimethylamino(naphth-1-yl)methylcyclopentadienide (206 mg, 0.49 mmol) in pentane (10 mL) dropwise at ambient temperature. Within 24 h the mixture changed from pale salmon to an intense red, while the amount of insolubles decreased. The solids were removed by centrifugation, and the solvent was evaporated in vacuo to leave behind 114 mg (0.21 mmol, 42%) of a red, crystalline solid. Anal. Calcd for C<sub>30</sub>H<sub>42</sub>BrNNi: C, 64.89; H, 7.62. Found: C, 64.12; H, 7.59. <sup>1</sup>H NMR (600 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ 7.65–7.85 (br, 7H, naphthyl), 7.35-7.55 (br, 7H, naphthyl), 5.18 (s, 1H, CHNMe<sub>2</sub>C<sub>10</sub>H<sub>7</sub>), 5.13 (s, 1H, CHNMe<sub>2</sub>C<sub>10</sub>H<sub>7</sub>), 3.69 (sep, 1H,  ${}^{3}J_{H,H} = 7.00$ , CH(CH<sub>3</sub>)<sub>2</sub>), 3.52 (sep, 1H,  ${}^{3}J_{H,H} = 7.32$ ,  $CH(CH_{3})_{2}$ ), 3.44 (s, 3H, NCH<sub>3</sub>), 3.32 (s, 3H, NCH<sub>3</sub>), 2.55 (br, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.46 (s, 6H, NCH<sub>3</sub>), 1.72 (sep, 1H,  ${}^{3}J_{\mathrm{H,H}} = 7.56, CH(CH_{3})_{2}), 1.56$  (d, 3H,  ${}^{3}J_{\mathrm{H,H}} = 7.00, CH(CH_{3})_{2}), 1.55$  (d, 3H,  ${}^{3}J_{\mathrm{H,H}} = 7.00, CH(CH_{3})_{2}), 1.50$  (d, 6H,  ${}^{3}J_{\mathrm{H,H}} = 7.33,$  $CH(CH_3)_2)$ , 1.46 (d, 3H,  ${}^{3}J_{H,H} = 7.14$ ,  $CH(CH_3)_2)$ , 1.42 (d, 3H,  ${}^{3}J_{H,H}$ = 7.56,  $CH(CH_3)_2$ ), 1.40 (d, 3H,  ${}^{3}J_{H,H}$  = 7.32,  $CH(CH_3)_2$ ), 1.39 (d, 3H,  ${}^{3}J_{H,H}$  = 7.32, CH(CH<sub>3</sub>)<sub>2</sub>), 1.38 (d, 3H,  ${}^{3}J_{H,H}$  = 6.60, CH(CH<sub>3</sub>)<sub>2</sub>), 1.37 (d, 3H,  ${}^{3}J_{H,H} = 7.00$ , CH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (d, 3H,  ${}^{3}J_{H,H} = 6.35$ , CH(CH<sub>3</sub>)<sub>2</sub>), 1.30 (d, 3H,  ${}^{3}J_{H,H} = 6.70$ , CH(CH<sub>3</sub>)<sub>2</sub>), 1.26 (d, 3H,  ${}^{3}J_{H,H} = 7.00$ , CH(CH<sub>3</sub>)<sub>2</sub>), 1.26 (d, 3H,  ${}^{3}J_{H,H} = 7.00$ , CH(CH<sub>3</sub>)<sub>2</sub>), 1.22 (d, 3H,  ${}^{3}J_{H,H} = 7.00$ , CH(CH<sub>3</sub>)<sub>2</sub>), 1.00 (d, 3H,  ${}^{3}J_{H,H} = 7.00$ , CH(CH<sub>3</sub>)<sub>2</sub>), 0.98 (d, 3H,  ${}^{3}J_{H,H} = 7.38$ , CH(CH<sub>3</sub>)<sub>3</sub>), 0.98 (d, 3H, {}^{3}J\_{H,H} = 7.38, CH(CH<sub>3</sub>)<sub>3</sub>), 0.9  $CH(CH_3)_2$ ), 0.97 (d, 3H,  ${}^{3}J_{H,H} = 6.35$ ,  $CH(CH_3)_2$ ), 0.94 (d, 3H,  ${}^{3}J_{H,H} = 6.35$ ,  $CH(CH_3)_2$ ), 0.94 (d, 3H,  ${}^{3}J_{H,H} = 6.35$ ,  $CH(CH_3)_2$ ).  ${}^{13}C{}^{1}H$ } NMR ( $C_6D_6$ ):  $\delta$  138.9 (naphthyl), 134.4 (naphthyl), 134.2 (naphthyl), 133.8 (naphthyl), 132.8 (naphthyl), 129.0 (naphthyl), 128.9 (naphthyl), 127.0 (naphthyl), 126.7 (naphthyl), 126.0 (naphthyl), 125.8 (naphthyl), 125.7 (naphthyl), 125.6 (naphthyl), 125.5 (naphthyl), 125.4 (naphthyl), 125.4 (naphthyl), 125.1 (naphthyl), 125.0 (naphthyl), 124.9 (naphthyl), 124.0 (naphthyl), 72.0 (C3 of Cp ring), 64.1 (C2 of Cp ring), 58.5 (C1 of Cp ring), 58.2 (C1 of Cp ring), 44.9 (NCH<sub>3</sub>), 44.6 (NCH<sub>3</sub>), 34.2 (CHMe<sub>2</sub>), 33.0 (isopropyl CH<sub>3</sub>), 32.9 (isopropyl CH<sub>3</sub>), 28.0 (CHMe2), 27.7 (CHMe2), 27.6 (CHMe2), 27.0 (CH(NMe2)-(naphthyl)), 26.9 (CHMe<sub>2</sub>), 26.6 (CHMe<sub>2</sub>), 26.2 (CHMe<sub>2</sub>), 23.7 (isopropyl CH<sub>3</sub>), 22.9 (isopropyl CH<sub>3</sub>), 22.8 (isopropyl CH<sub>3</sub>), 22.7 (isopropyl CH<sub>3</sub>), 22.6 (isopropyl CH<sub>3</sub>), 22.5 (isopropyl CH<sub>3</sub>), 22.1 (isopropyl CH<sub>3</sub>), 21.9 (isopropyl CH<sub>3</sub>), 21.2 (isopropyl CH<sub>3</sub>), 20.8 (isopropyl CH<sub>3</sub>), 14.0 (isopropyl CH<sub>3</sub>), 13.9 (isopropyl CH<sub>3</sub>).

#### ASSOCIATED CONTENT

#### **Supporting Information**

CIF files giving crystallographic data for 8, 11, 13, 14, 16–18, and 20. This material is available free of charge via the Internet at http://pubs.acs.org.

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