

## Monomeric Nickel(II) Amido Complexes. Synthesis, Reactivity, and Dynamics

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Addition of KNHAr to *trans*-Ni(PMe<sub>3</sub>)<sub>2</sub>(Ar')Cl (Ar = Ph, 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; Ar' = Ph, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) results in the formation of monomeric Ni(II) amide complexes of the type *trans*-Ni(PMe<sub>3</sub>)<sub>2</sub>(NHAr)(Ar') in good yield, with the exception of the amide complex *trans*-Ni(PMe<sub>3</sub>)<sub>2</sub>(NHPH)(Ph), **1a**, which is initially formed as a mixture of monomer, **1a**, and dimeric compounds (which form upon loss of PMe<sub>3</sub>), **1b**. The monomer and dimers can be readily interconverted by the addition or removal of PMe<sub>3</sub>. The compounds *trans*-Ni(PMe<sub>3</sub>)<sub>2</sub>(NHAr')(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) react readily with H<sub>2</sub>O to form the binuclear hydroxide compound [Ni( $\mu$ -OH)(PMe<sub>3</sub>)(Mes)]<sub>2</sub>, **5**. The compound *trans*-Ni(PMe<sub>3</sub>)<sub>2</sub>(NHPH)(Mes), **3**, reacts with a variety of small electrophilic molecules resulting in insertion into either the Ni–N bond or the N–H bond. A single-crystal X-ray diffraction study of *trans*-Ni(PMe<sub>3</sub>)<sub>2</sub>(Mes)-[N(Ph)C(O)CHPh<sub>2</sub>], **8**, which resulted from the addition of diphenylketene to **3**, reveals that it crystallizes in the space group *P2<sub>1</sub>/c* with *a* = 9.379(1) Å, *b* = 19.561(2) Å, *c* = 18.793(2) Å,  $\beta$  = 103.07(1)°, *V* = 3358.5(6) Å<sup>3</sup>, and *Z* = 4. A short N–C<sub>carbonyl</sub> bond length of 1.354(3) Å reveals that nitrogen's lone pair of electrons is delocalized onto the carbonyl, stabilizing the complex. All but one of the insertion or addition products of **3** exhibit a hindered rotation about the Ni–R bond in the compounds *trans*-Ni(PMe<sub>3</sub>)<sub>2</sub>(Mes)R. The  $\Delta G^\ddagger$  for rotation of the Ni–R bonds in these compounds was measured using variable-temperature NMR experiments and can be correlated with the steric bulk of the R group.

## Introduction

The chemistry of late transition metal amide complexes (groups 8–10) has received a great deal of attention in recent years because of the potential for these complexes to facilitate carbon–nitrogen bond formation.<sup>1,2</sup> While the formation of carbon–nitrogen bonds via the insertion of small, unsaturated, electrophilic molecules into M–NR<sub>2</sub> bonds has been demonstrated,<sup>3</sup> the question of whether or not M–NR<sub>2</sub> complexes can mediate C–N bond formation as readily as metal alkyl complexes mediate C–C bond formation is still an open issue. The development of the chemistry of late transition metal amide complexes has been hindered by the inability of the electronically saturated metal center to accept  $\pi$ -donation from the lone pair of electrons of the amide moiety.<sup>4</sup> Since it now appears as though the reactivity of the amide complex will be governed by the lone pair of electrons on the amide nitrogen, structural information is essential. Currently, few structure determinations of late transition metal amide complexes have been reported.

Although amide complexes of the Ni triad are becoming more common,<sup>5</sup> a firm grasp of the stability and reactivity of these compounds has not been established. In this paper, we report the preparation of four new nickel(II) amide complexes having the general formula *trans*-Ni(PMe<sub>3</sub>)<sub>2</sub>(Ar)(NHAr') (Ar = Ph, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; Ar' = Ph, 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). The reactions of *trans*-Ni(PMe<sub>3</sub>)<sub>2</sub>(mesityl)(NHPH), **3**, with an assortment of small unsaturated molecules are discussed as are the structural and spectroscopic features of both the amide complexes and the reaction products.

## Results and Discussion

The nickel(II) amide complexes described in this paper are all orange to red crystalline compounds, which are extremely air and moisture sensitive. They are thermally stable at room temperature and can be stored indefinitely under an inert atmosphere. Although lithium and sodium amide salts have been used to synthesize some late transition metal amide complexes, the potassium salts proved the most useful for the amide complexes described in this work. The <sup>1</sup>H NMR and <sup>31</sup>P{<sup>1</sup>H} NMR data for all of the compounds described can be found in Tables 1 and 2, respectively. A table of the <sup>13</sup>C{<sup>1</sup>H} NMR data can be found in the Supporting Information.

**Reaction of *trans*-Ni(Ph)(PMe<sub>3</sub>)<sub>2</sub> with KNHAr (Ar = Ph, 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).** The compound *trans*-NiBr(Ph)(PMe<sub>3</sub>)<sub>2</sub> reacts

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Table 1. <sup>1</sup>H NMR Spectroscopic Data<sup>a</sup>

compound	δ, ppm	mult	J <sub>H-H</sub> , Hz	integ	assignt	compound	δ, ppm	mult	J <sub>H-H</sub> , Hz	integ	assignt
<i>trans</i> -Ni(Ph)(NHPH)-(PMe <sub>3</sub> ) <sub>2</sub> ( <b>1a</b> )	0.18	s		1	-NH	<i>trans</i> -Ni(Mes)-(OC(O)NHPH)-(PMe <sub>3</sub> ) <sub>2</sub> ( <b>6</b> )	0.97	t	4 <sup>b</sup>	18	<i>trans</i> -PMe <sub>3</sub>
	0.67	s		18	<i>trans</i> -PMe <sub>3</sub>		2.13	s		3	Mes- <i>p</i> -Me
	6.54	t	7	1	aromatic		2.95	s		6	Mes- <i>o</i> -Me
	6.86	t	7	1	aromatic		6.50	s		2	aromatic
	6.99	d	7	2	aromatic		6.68	s		1	-NH
	7.02	t	7	2	aromatic		6.84	t	7	1	aromatic
	7.27	t	7	2	aromatic		7.20	t	8	2	aromatic
[Ni(Ph)(μ-NHPH)-(PMe <sub>3</sub> ) <sub>2</sub> ] ( <b>1b</b> )	7.39	d	7	2	aromatic	7.40	d	8	2	aromatic	
	-0.87	s			-N-H	<i>trans</i> -Ni(Mes)[C(CO <sub>2</sub> Me)-C(CO <sub>2</sub> Me)NHPH]-(PMe <sub>3</sub> ) <sub>2</sub> ( <b>7</b> )	0.82	t	4 <sup>b</sup>	18	<i>trans</i> -PMe <sub>3</sub>
	-0.76	s			-N-H		2.25	s		3	Mes- <i>p</i> -Me
	-0.41	s			-N-H		2.58	s		3	Mes- <i>o</i> -Me
	0.19	d	9 <sup>b</sup>		PMe <sub>3</sub>		2.62	s		3	Mes- <i>o</i> -Me
	0.31	d	9 <sup>b</sup>		PMe <sub>3</sub>		3.49	s		3	-CO <sub>2</sub> CH <sub>3</sub>
	0.41	d	9 <sup>b</sup>		PMe <sub>3</sub>		3.62	s		3	-CO <sub>2</sub> CH <sub>3</sub>
	6.75-7.88				aromatic		6.43	s		1	-NH
<i>trans</i> -Ni(Ph)-(NH(2,6- <sup>1</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ))-(PMe <sub>3</sub> ) <sub>2</sub> ( <b>2</b> )	0.20	s			-NH	6.69	s		1	aromatic	
	0.64	t	4 <sup>b</sup>	18	<i>trans</i> -PMe <sub>3</sub>	6.71	s		1	aromatic	
	1.49	d	7	12	-CH(CH <sub>3</sub> ) <sub>2</sub>	6.76	t	7	1	aromatic	
	4.77	m	7	2	-CH(CH <sub>3</sub> ) <sub>2</sub>	6.85	d	7	2	aromatic	
	6.67	t	7	1	aromatic	7.17	t	7	2	aromatic	
	6.86	t	7	1	aromatic	<i>trans</i> -Ni(Mes)[N(Ph)-C(O)CHPh <sub>2</sub> -(PMe <sub>3</sub> ) <sub>2</sub> ] ( <b>8</b> )	0.50	t	4 <sup>b</sup>	18	<i>trans</i> -PMe <sub>3</sub>
	7.01	t	8	2	aromatic		2.22	s		3	Mes- <i>p</i> -Me
7.16	d	8	2	aromatic	3.06		s		6	Mes- <i>o</i> -Me	
7.44	d	7	2	aromatic	5.68				1	CH <sub>2</sub> Ph <sub>2</sub>	
<i>trans</i> -Ni(Mes)(NHPH)-(PMe <sub>3</sub> ) <sub>2</sub> ( <b>3</b> )	0.03	s		1	-NH		6.64			2	aromatic
	0.63	t	3 <sup>b</sup>	18	<i>trans</i> -PMe <sub>3</sub>		6.91-7.39			11	aromatic
	2.26	s		3	Mes- <i>p</i> -Me		<i>trans</i> -Ni(Mes)[N(Ph)-C(O)NHPH]-(PMe <sub>3</sub> ) <sub>2</sub> ( <b>9</b> )	0.87	t	3 <sup>b</sup>	18
	2.83	s		6	Mes- <i>o</i> -Me	2.17		s		3	Mes- <i>p</i> -Me
	6.52	t	7	1	aromatic	2.88		s		3	Mes- <i>o</i> -Me
	6.68	s		2	aromatic	3.01		s		3	Mes- <i>o</i> -Me
	6.89	d	6	2	aromatic	6.61		s		1	Mes- <i>p</i> -H
7.26	t	7	2	aromatic	6.63	s			1	Mes- <i>p</i> -H	
<i>trans</i> -Ni(Mes)-(NH(2,6- <sup>1</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ))-(PMe <sub>3</sub> ) <sub>2</sub> ( <b>4</b> )	0.39	s		1	-NH	6.85		t		1	aromatic
	0.63	t	3 <sup>b</sup>	18	<i>trans</i> -PMe <sub>3</sub>	6.93	t		1	aromatic	
	1.43	d	7	12	-CH(CH <sub>3</sub> ) <sub>2</sub>	7.28	mm		4	aromatic	
	2.23	s		3	Mes- <i>p</i> -Me	7.58	d		2	aromatic	
	2.83	s		6	Mes- <i>o</i> -Me	8.01	d		2	aromatic	
	4.23	s		2	-CH(CH <sub>3</sub> ) <sub>2</sub>	8.04	s		1	-NH	
	6.65	s		2	aromatic	<i>trans</i> -Ni(Mes)[N(Ph)-C(O)NHCMe <sub>3</sub> ]-(PMe <sub>3</sub> ) <sub>2</sub> ( <b>10</b> )	0.65	t	4 <sup>b</sup>	18	<i>trans</i> -PMe <sub>3</sub>
6.70	t	7	1	aromatic	1.52		s		9	-CMe <sub>3</sub>	
7.13	d	7	2	aromatic	2.23		s		3	Mes- <i>p</i> -Me	
[Ni(Ph)(μ-OH)-(PMe <sub>3</sub> ) <sub>2</sub> ] ( <b>5</b> )	-3.78	s		2	μ-OH		2.89	s		3	Mes- <i>o</i> -Me
	0.38	d	9 <sup>b</sup>	18	PMe <sub>3</sub>		3.07	s		3	Mes- <i>o</i> -Me
	2.24	s		6	Mes- <i>p</i> -Me		5.37	s		1	-NH
	3.56	s		12	Mes- <i>o</i> -Me		6.67	s		2	aromatic
	6.73	s		4	aromatic	6.84	t		1	aromatic	
					7.31	t		2	aromatic		
					8.12	d		2	aromatic		

<sup>a</sup> All spectra were recorded in C<sub>6</sub>D<sub>6</sub>. <sup>b</sup> Measured peak separations for virtual multiplets.

Table 2. <sup>31</sup>P{<sup>1</sup>H} NMR Spectroscopic Data<sup>a</sup>

compd	δ, Hz <sup>b</sup>	compd	δ, Hz <sup>b</sup>	compd	δ, Hz <sup>b</sup>
<b>1a</b>	-14.73	<b>3</b>	-14.99	<b>7</b>	-11.75
<b>1b</b>	-9.85	<b>4</b>	-18.07	<b>8</b>	-17.12
<b>1b</b>	-12.37	<b>5</b>	-6.61	<b>9</b>	-14.78
<b>1b</b>	-15.64	<b>6</b>	-14.88	<b>10</b>	-14.61
<b>2</b>	-16.51				

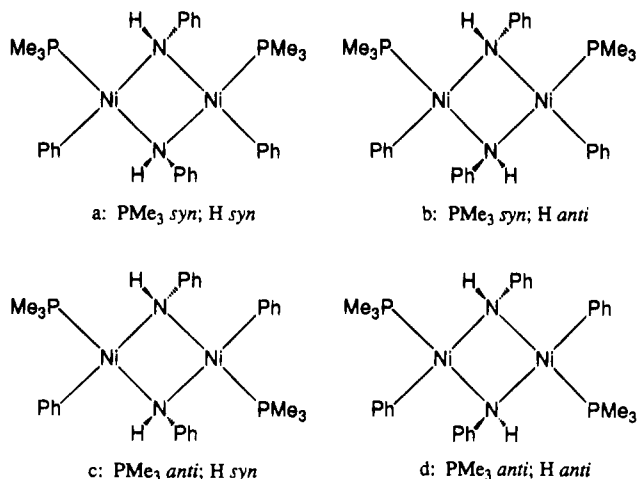
<sup>a</sup> All spectra were recorded in C<sub>6</sub>D<sub>6</sub>. <sup>b</sup> All of the resonances were singlets.

with a small excess of KNHPH to afford a yellow solid which is a mixture of monomeric amide and three dimeric species. Four sharp singlets were observed in the <sup>31</sup>P{<sup>1</sup>H}NMR while in the <sup>1</sup>H NMR a broad singlet and three doublets were observed for the PMe<sub>3</sub> protons corresponding to the presence of *trans*-Ni(Ph)(NHPH)(PMe<sub>3</sub>)<sub>2</sub>, **1a**, and three isomers of [Ni(Ph)(μ-NHPH)(PMe<sub>3</sub>)<sub>2</sub>], **1b**. The stoichiometry of **1b** gives rise to four possible isomers as shown in Figure 1. There are two isomers with the phosphine groups *syn* to one another and two isomers with the phosphine groups *anti* to one another. In both isomers

it is possible that the *N*- and *N'*-phenyl groups of the two bridging amido groups are either *syn* or *anti* with respect to one another.

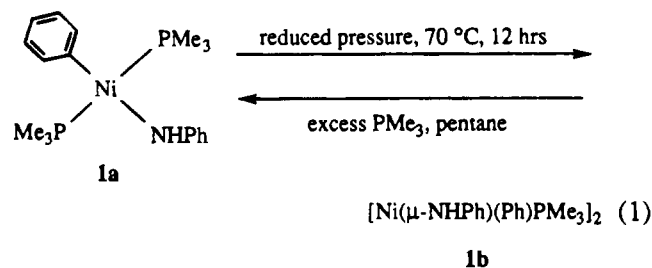
The initial product mixture can be converted into either pure monomeric or pure dimeric products. Heating the solid, crude product to 70 °C under reduced pressure for 24 h led to complete conversion of **1a** to dimeric products **1b**. The resonance attributed to **1a** in the <sup>31</sup>P{<sup>1</sup>H} NMR of the initial reaction mixture (observed at -14.73 ppm) was no longer present. Three dimeric amides were still present as evidenced by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR. Three doublets, corresponding to the phosphine methyl groups were observed in the <sup>1</sup>H NMR as well as three broad singlets at -0.41, -0.76, and -0.87 ppm corresponding to the NH protons. Using the integration from the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, the sharp singlets at -9.85, -12.37, and -15.64 ppm were observed to be in a 5:10:2 ratio. Assignment of these resonances to individual isomers has not been possible.

A mixture of dimers can be converted to monomer by addition of excess ligand. Addition of excess PMe<sub>3</sub> to an NMR sample



**Figure 1.** The four possible configurations for  $[\text{Ni}(\mu\text{-NHPh})(\text{Ph})(\text{PMe}_3)_2]_2$ , **1b**.

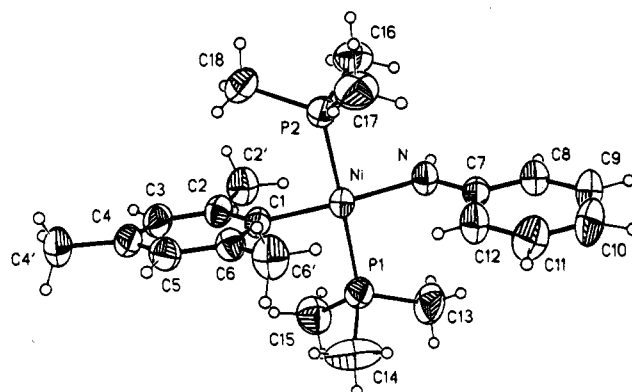
of a mixture of **1a** and **1b** resulted in conversion to a single product with a singlet at  $-14.73$  ppm in the  $^{31}\text{P}$  NMR spectrum (free  $\text{PMe}_3$  is also observed). Isolation of pure **1a** was achieved by addition of greater than 2 equiv of neat  $\text{PMe}_3$  to a pentane solution of **1a** and **1b** followed by cooling to  $-10$  °C for 72 h. Red-orange crystals of **1a** were isolated by filtration and dried under a flow of argon to prevent  $\text{PMe}_3$  loss which was observed under reduced pressure. The reversibility of the monomer-dimer transformation is shown in eq 1. The ratio of monomer



to dimers in the initial reaction mixture is dependent on the length of time the residue and product are exposed to reduced pressure. However, the ratio of the dimeric isomers to one another, **1b**, is consistent regardless of the monomer-dimer distribution.

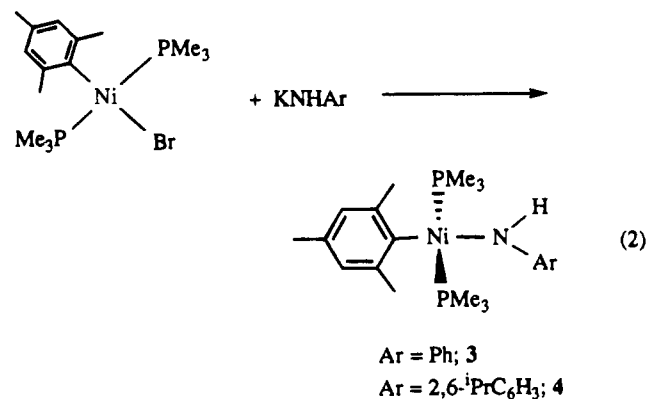
The tendency of **1a** to dimerize is an undesirable characteristic for the study of the reactivity of Ni-N bonds, although it is consistent with Klein's observations for  $[\text{Ni}(\text{Me})(\mu\text{-NHR})(\text{PMe}_3)_2]$ , R = Ph, Me, in which only dimeric products were isolated.<sup>6</sup> In an attempt to increase steric bulk, and decrease the tendency for dimerization, *trans*- $\text{NiBr}(\text{Ph})(\text{PMe}_3)_2$  was allowed to react with an excess of  $\text{KNH}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$  at  $-78$  °C to give *trans*- $\text{Ni}(\text{Ph})(\text{NH}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3))(\text{PMe}_3)_2$ , **2**. A triplet observed at 0.64 ppm in the  $^1\text{H}$  NMR and a singlet observed at  $-16.51$  ppm in the  $^{31}\text{P}$  NMR both confirm the *trans* geometry of **2**. The NH proton was observed at 0.20 ppm in the  $^1\text{H}$  NMR. When **2** was heated to 70 °C under reduced pressure, some decomposition occurred, but no dimer formation was observed by  $^1\text{H}$  NMR.

**Reaction of *trans*- $\text{NiBr}(\text{Mes})(\text{PMe}_3)_2$  with  $\text{KNHAr}$  (Ar = Ph, 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$ ).** The effect of ancillary steric bulk on dimer formation was investigated by using *trans*- $\text{NiBr}(\text{Mes})(\text{PMe}_3)_2$  (Mes = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$ ) as the starting material. The ease of preparation of *trans*- $\text{NiBr}(\text{Mes})(\text{PMe}_3)_2$  over *trans*- $\text{NiBr}(\text{Ph})$ -



**Figure 2.** Thermal ellipsoid plot of *trans*- $\text{Ni}(\text{Mes})(\text{NHPH})(\text{PMe}_3)_2$ , **3**. Selected bond lengths, Å: N-H, 0.82(2); Ni-N, 1.932(3); N-C7, 1.354(5); Ni-C1, 1.910(4); Ni-P1, 2.1896(10); Ni-P2, 2.1824(11). Selected bond angles, deg: P1-Ni-P2, 177.78(8); N-Ni-C1, 175.73(13); C7-N-Ni, 129.9(2).

( $\text{PMe}_3$ )<sub>2</sub> was also expedient. *Ortho*-disubstituted aryl groups are known to stabilize square-planar *trans*- $\text{Ni}(\text{PR}_3)_2(\text{Ar})\text{X}$  complexes.<sup>7</sup> Since the *ortho* substituents hinder the rotation of the mesityl ring about the M-C bond, they force an orientation of the mesityl ring in which the *ortho* substituents protect the metal center from nucleophilic attack. The compounds *trans*- $\text{Ni}(\text{Mes})(\text{NHPH})(\text{PMe}_3)_2$ , **3**, and *trans*- $\text{Ni}(\text{Mes})(\text{NH}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3))(\text{PMe}_3)_2$ , **4**, were prepared similarly to **2** (eq 2). NMR data



confirm that **3** and **4** are both monomers in the *trans* configuration. The  $\text{PMe}_3$  ligands provided an excellent diagnostic probe for the confirmation of the square planar geometry of these complexes. In the  $^{31}\text{P}$  NMR of **3**, a singlet was observed at  $-14.99$  ppm while a virtual triplet at 0.63 ppm was observed in the  $^1\text{H}$  NMR, confirming that the phosphine ligands are *trans* to one another. Similarly, the observation of a singlet at  $-18.07$  ppm in the  $^{31}\text{P}$  NMR spectrum and a triplet at 0.63 ppm in the  $^1\text{H}$  NMR spectrum of **4** also confirmed the *trans* geometry of the phosphines. The NH resonances are observed as broad singlets at 0.03 and 0.39 ppm for **3** and **4**, respectively.

**Structure of *trans*- $\text{Ni}(\text{Mes})(\text{NHPH})(\text{PMe}_3)_2$ , **3**.** The X-ray structure of **3**, Figure 2, was recently reported.<sup>8</sup> The coordination geometry of the Ni atom is square planar with the mesityl ring oriented perpendicular to the plane of coordination. The Ni-N bond length was found to be relatively short, at 1.932(3) Å. The geometry about the nitrogen was shown to be planar because the amide proton was located in the difference Fourier map and refined without constraints. The lone pair of electrons

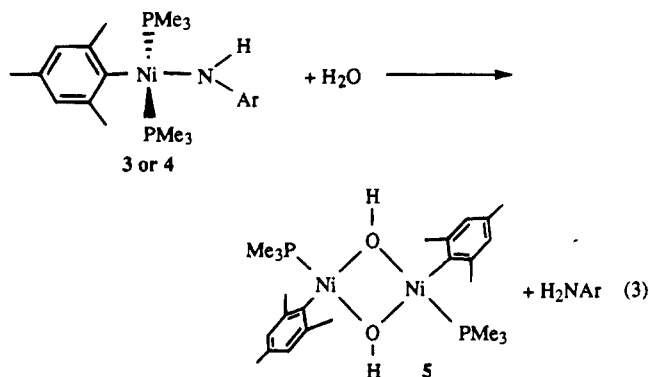
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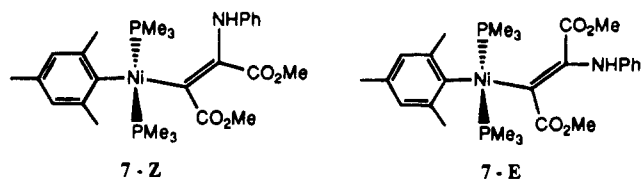
is delocalized onto the phenyl ring as is evidenced by the short N–C<sub>phenyl</sub> bond length of 1.354(5) Å. Short N–C<sub>phenyl</sub> bond lengths, of 1.32(2) and 1.388(10) Å are also observed in the related compounds *trans*-Pd(Ph)(NHPH)(PMe<sub>3</sub>)<sub>2</sub><sup>5g</sup> and *trans*-Ir(NH-*p*-C<sub>6</sub>H<sub>4</sub>Me)(CO)(PPh<sub>3</sub>)<sub>2</sub><sup>5e</sup> respectively. The aptitude of nitrogen's lone pair of electrons to delocalize onto the phenyl ring is likely the reason for the stability of **3**. That very few non-aryl-substituted late transition metal amides have been isolated may be due to the fact that the lone pair of electrons are too reactive.<sup>5a,f</sup> Stabilization of the amide by delocalization of nitrogen's lone pair onto a phenyl ring is helpful, though not absolutely necessary.<sup>5f</sup>

**Reaction of 3 and 4 with H<sub>2</sub>O.** The rapid color change observed from red to yellow when either **3** or **4** was exposed to the atmosphere in the solid state prompted further investigation. When Et<sub>2</sub>O solutions of compounds **3** and **4** were allowed to react with 1 equiv of H<sub>2</sub>O and the mixtures were cooled to –10 °C, a yellow crystalline solid was isolated (eq 3). The <sup>1</sup>H NMR



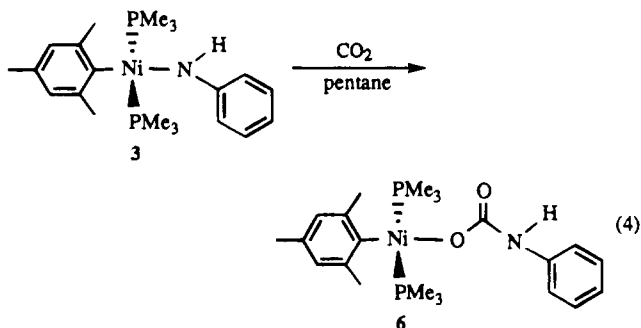
spectrum of the product, **5**, reveals a doublet at 0.38 ppm that is assigned to the PMe<sub>3</sub> protons. There is a singlet at –3.87 ppm that we assign to the OH proton by analogy with [Ni(R)(μ-OH)(PMe<sub>3</sub>)<sub>2</sub>] (R = Me, CH<sub>2</sub>CMe<sub>2</sub>Ph, CH<sub>2</sub>SiMe<sub>3</sub>).<sup>9,10</sup> In the IR spectrum of **5** there is an absorption at 3658 cm<sup>–1</sup> that is assigned to ν<sub>O–H</sub>. These data are consistent with formulation of the product as [Ni(Mes)(μ-OH)(PMe<sub>3</sub>)<sub>2</sub>]. Observation of one singlet at –3.87 ppm in the <sup>1</sup>H NMR confirms that the product has the phosphine ligands *anti* to one another. No *syn* product is observed, which would result in the presence of two upfield singlets. Variable-temperature NMR experiments over the temperature range –50 to +90 °C do not reveal any isomerization. Addition of PMe<sub>3</sub> does not promote *syn/anti* isomerization or the formation of a monomeric hydroxide complex of the type Ni(Mes)(OH)(PMe<sub>3</sub>)<sub>2</sub>. Similar hydroxide-bridged compounds have been prepared by Klein<sup>9</sup> and Carmona<sup>10</sup> by the addition of NaOH to NiCl(R)(PR'<sub>3</sub>)<sub>2</sub>. An equilibrium mixture of *syn* and *anti* products was observed for [Ni(R)(μ-OH)(PMe<sub>3</sub>)<sub>2</sub>] (R = Me, CH<sub>2</sub>CMe<sub>2</sub>Ph, CH<sub>2</sub>SiMe<sub>3</sub>), while only the *anti* configuration of [Ni(CH<sub>2</sub>Ph)(μ-OH)(PMe<sub>3</sub>)<sub>2</sub>] was observed.<sup>10</sup> The hydroxide protons in these compounds are also responsible for <sup>1</sup>H NMR resonances in the range –1.5 to –5 ppm.<sup>9,10</sup>

**Reactions of *trans*-Ni(Mes)(NHPH)(PMe<sub>3</sub>)<sub>2</sub>, **3**, with Electrophiles.** Although compounds **1–4** react with electrophiles, the reactivity of **3** has been most thoroughly investigated due to the ease of isolation of both the amide complex and the reaction products. When CO<sub>2</sub> is bubbled through a pentane solution of *trans*-Ni(Mes)(NHPH)(PMe<sub>3</sub>)<sub>2</sub>, **3**, a yellow solid



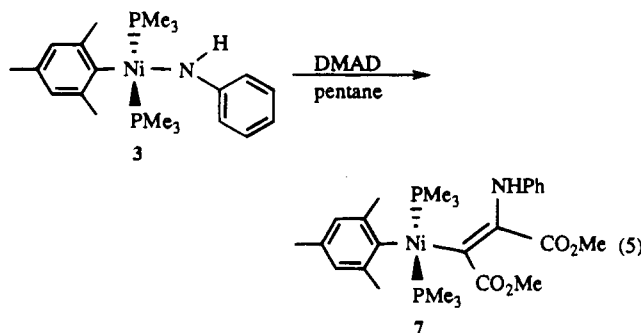
**Figure 3.** The E and Z isomers of *trans*-Ni(Mes)[C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)NHPH](PMe<sub>3</sub>)<sub>2</sub>, **7**.

precipitates from solution, and additional solid is isolated upon cooling the reaction mixture to –10 °C (eq 4). The <sup>1</sup>H NMR



spectrum reveals a shift in the NH resonance from 0.03 to 6.68 ppm and indicates the formation of the carbamate NH of the product *trans*-Ni(Mes)(OC(O)NHPH)(PMe<sub>3</sub>)<sub>2</sub>, **6**. A triplet at 0.97 ppm in the <sup>1</sup>H NMR and a singlet at –14.88 ppm in the <sup>31</sup>P NMR confirm that **6** is the *trans* isomer. This structure is also supported by the appearance of a new absorption in the IR at 1634 cm<sup>–1</sup> which is assigned to the ν<sub>CO</sub> of the carbamate functional group. The observation of the insertion of CO<sub>2</sub> into the M–N bond, forming the carbamate, is consistent with previously reported work involving other late transition metal amides.<sup>3d,11a,12</sup>

Insertion into the nickel–nitrogen bond also occurs when CH<sub>3</sub>O<sub>2</sub>CC≡CCO<sub>2</sub>CH<sub>3</sub>, DMAD, is added to a pentane solution of **3**. Cooling the solution to –10 °C affords crystals of *trans*-Ni(Mes)[C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)NHPH](PMe<sub>3</sub>)<sub>2</sub>, **7** (eq 5). The <sup>1</sup>H



NMR reveals a shift in the NH resonance similar to the spectrum of **6**. The PMe<sub>3</sub> ligands are observed as a triplet at 0.82 ppm in the <sup>1</sup>H NMR, confirming that the product is in the *trans* configuration. The two possible configurations of the insertion product, E and Z forms, can be seen in Figure 3.

From the results of NOE experiments, it can be concluded that the C=C bond substituents are in the Z configuration. When the NH proton is irradiated, an enhancement of 3.1% is observed

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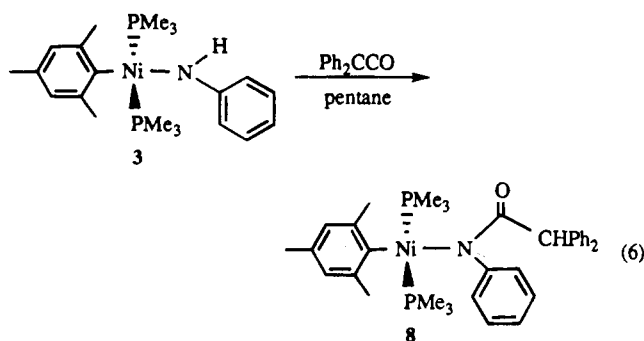
(10) (a) Carmona, E.; Marin, J. M.; Palma, P.; Paneque, M.; Poveda, M. *Inorg. Chem.* **1989**, *28*, 1895. (b) Carmona, E.; Marin, J. M.; Paneque, M.; Poveda, M. *Organometallics* **1987**, *6*, 1757.

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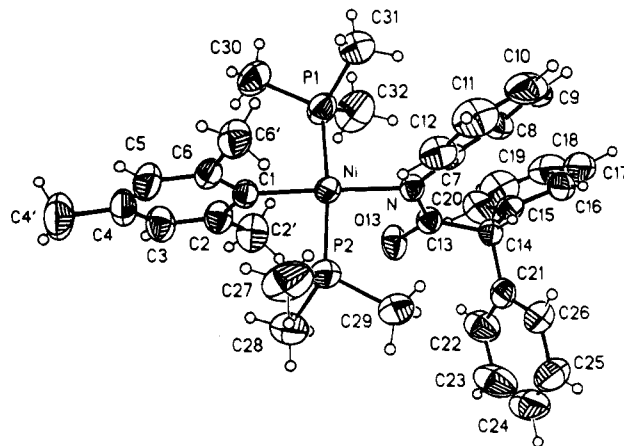
for the *ortho* mesityl methyl group, while no enhancement is observed, <0.5%, for either carboxylate methyl. Additionally, a 2.6% enhancement of the  $\alpha$ -carboxylate upon irradiation of the  $\text{PMe}_3$  methyls is observed, with no enhancement of the  $\beta$ -carboxylate. These results are similar to those observed for an analogous palladium complex, *trans*-Pd(Ph)[C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)NHPh](PMe<sub>3</sub>)<sub>2</sub>, which has been structurally characterized and found to exist in the *Z* configuration.<sup>2d</sup> The methyl groups in the *ortho* positions on the mesityl group in **7** are inequivalent in both the <sup>1</sup>H and <sup>13</sup>C NMR. For these methyl groups to be inequivalent, there must be hindered rotation about both the Ni–mesityl and Ni–(C=C) bonds. This hindered rotation will be discussed in detail below.

A result similar to those of eqs 3 and 4 would be expected for the insertion of Ph<sub>2</sub>CCO into the Ni–N bond of **3**. However, N–H addition to the ketene was observed (eq 6) forming *trans*-



Ni(Mes)[N(Ph)C(O)CHPh<sub>2</sub>](PMe<sub>3</sub>)<sub>2</sub>, **8**. A singlet was observed at 5.68 ppm corresponding to the new –CHPh<sub>2</sub> proton. Also, the N–H stretch which appeared at 3331 cm<sup>–1</sup> for **3** was no longer present. The *trans* coordination geometry of **8** has been confirmed by the observation of a triplet at 0.50 ppm in the <sup>1</sup>H NMR and a sharp singlet at –17.12 ppm in the <sup>31</sup>P NMR. The *ortho* mesityl methyl groups were observed as a broad singlet at 3.06 ppm in the <sup>1</sup>H NMR at 25 °C. The broad signal indicated that the two methyl groups were exchanging slowly on the NMR time scale. At –30 °C, the broad singlet separated into two sharp singlets, indicating that the methyl groups became inequivalent. The same phenomenon was observed for the *meta* mesityl protons. This inequivalence was a result of a hindered rotation of the Ni–Mes bond and the Ni–N bond similar to that observed in **7**.

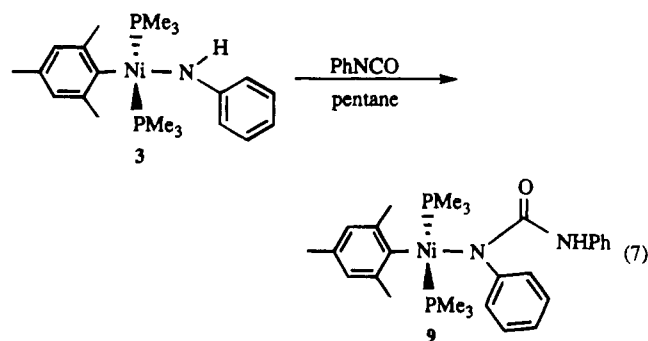
**Structure of Ni(Mes)[N(Ph)C(O)CHPh<sub>2</sub>](PMe<sub>3</sub>)<sub>2</sub>.** When the crude reaction mixture of **3** and Ph<sub>2</sub>CCO in pentane was cooled to –10 °C, large orange crystals of **8** were isolated. The crystals were cleaved and mounted for an X-ray structure determination, the results of which are shown in Figure 4. Crystallographic data and thermal parameters can be found in Tables 3 and 4, respectively. Selected bond lengths and angles can be found in Table 5. The structure of **8** consists of square planar coordination around the nickel metal center with the phosphines *trans* to one another. Similar to the structure of **3**, the mesityl ring is oriented perpendicular (89.2°) to the coordination plane defined by P1, P2, N, and C<sub>mesityl</sub>. The Ni–N bond length is 1.974(5) Å. This is a lengthening of 0.04 Å from **3**. The geometry around the nitrogen atom is essentially planar with the nitrogen atom lying only 0.04 Å from the plane defined by Ni, C7, and C13. In compound **3**, the lone pair of electrons from the nitrogen is delocalized onto the phenyl ring; in **8**, nitrogen's lone pair of electrons is delocalized onto the carbonyl group. A short N–C<sub>carbonyl</sub> bond length of 1.339(3) Å gives evidence for this interaction. The N–C<sub>phenyl</sub> distance is 1.419(5) Å in **8**, compared to 1.354(4) Å in **3**. This is also a reflection of the ability of the carbonyl group to delocalize



**Figure 4.** Thermal ellipsoid plot of *trans*-Ni(Mes)[N(Ph)C(O)CHPh<sub>2</sub>](PMe<sub>3</sub>)<sub>2</sub>, **8**. Thermal ellipsoids are drawn at the 50% probability level.

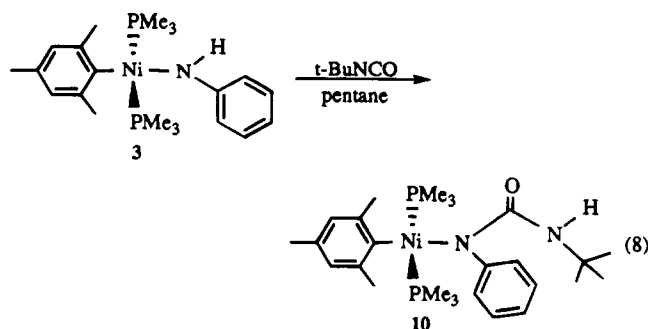
the lone pair through resonance stabilization to a much greater extent than the phenyl ring.

Insertion of isocyanates into either the M–N bond or the N–H bond of late transition metal amide complexes has been observed.<sup>3c–e,11a</sup> When **3** was allowed to react with 1 equiv of PhNCO (eq 7), it was not obvious from the product, *trans*-Ni-



(Mes)[N(Ph)C(O)NHPh](PMe<sub>3</sub>)<sub>2</sub> **9**, where the isocyanate inserted. The same product would have been formed in either case. The <sup>1</sup>H NMR of **9** reveals a downfield shift in the NH resonance was observed for **9**. At 25 °C the NH resonance was obscured by an aromatic doublet at 8.01 ppm; however, at –35 °C the NH was observed as a singlet at 8.52 ppm. The *ortho* mesityl methyls were inequivalent in the NMR, appearing as two singlet resonances in both the <sup>1</sup>H and <sup>13</sup>C NMR spectra at room temperature. <sup>15</sup>N-labeling experiments performed on the formation of the compound *trans*-Pd(Ph)[N(Ph)C(O)NHPh](PMe<sub>3</sub>)<sub>2</sub>, demonstrated that the isocyanate first inserts into the M–N bond but then rearranges to give the N–H insertion product.<sup>11a</sup>

When a pentane solution of **3** and 1 equiv of <sup>1</sup>BuNCO were mixed and cooled to –10 °C, yellow crystals of *trans*-Ni(Mes)-[N(Ph)C(O)NH<sup>1</sup>Bu](PMe<sub>3</sub>)<sub>2</sub>, **10**, were isolated (eq 8). The <sup>1</sup>H



**Table 3.** Crystallographic Data

$C_{35}H_{45}NOP_2Ni$	$P2_1/c$
$M_r = 616.37$	$T = 23\text{ }^\circ\text{C}$
$a = 9.379(1)\text{ \AA}$	$\lambda = 0.710\ 73\text{ \AA}$ (MoK $\alpha$ )
$b = 19.561(2)\text{ \AA}$	$\rho_{\text{calc}} = 1.219\text{ g cm}^{-3}$
$c = 18.793(2)\text{ \AA}$	$\mu = 0.70\text{ cm}^{-1}$
$\beta = 103.07(1)^\circ$	min, max transm: 0.806, 0.877
$V = 3358.5(6)\text{ \AA}^3$	$R(F_o)^a = 4.94\%$
$Z = 4$	$R_w(F_o)^b = 5.37\%$

$$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|, \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}.$$

NMR of **10** shows that the shift of the NH resonance, observed at 5.37 ppm, was much smaller than that for **9**. The insertion into the N–H bond was supported by the observed NOE enhancement of the NH resonance by irradiation of the <sup>t</sup>Bu methyls. An enhancement of 18.4% verifies that the H and <sup>t</sup>Bu group are bound to the same nitrogen. Inequivalence of the *ortho* mesityl methyls was observed in **10** by both the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

**Structure of *trans*-Ni(Mes)[N(Ph)C(O)NH<sup>t</sup>Bu](PMe<sub>3</sub>)<sub>2</sub>, **10**.** The structure of **10** has been previously reported.<sup>13</sup> The structure confirms that insertion into the N–H bond was preferred over insertion into the Ni–N bond, Figure 5. The geometry is similar to that observed in compounds **3** and **8**, with a square planar Ni atom and the mesityl group oriented perpendicular to the coordination plane. The Ni–N bond length is 1.978(6) Å, similar to that in **8**. The geometry around the amide nitrogen is planar, similar to that observed in **8**, as would be expected for a substituted urea derivative.

**Rotational Barriers of Compounds 10–14.** Throughout this paper, the inequivalence of *ortho* mesityl methyl groups has been noted. In order for these methyl groups to be chemically inequivalent, there must be hindered rotation about both the Ni–Mes bond and the Ni bond to the substituent *trans* to the Ni–Mes group (Figure 6). Rapid rotation of either of these groups on the NMR time scale will result in the chemical equivalence of the mesityl methyl groups. The activation barriers for the hindered rotation were measured by determining the coalescence temperature ( $T_c$ ) of the mesityl methyl groups and applying the two-site exchange approximation.<sup>14</sup> For compounds **7–10**, both the low- and high-temperature limiting spectra were observed. The  $\Delta G^\ddagger$  and  $T_c$  values are reported in Table 6. The values of  $\Delta G^\ddagger_{\text{rot}}$  for compounds **7**, **9**, and **10** are similar in magnitude while  $\Delta G^\ddagger_{\text{rot}}$  for **8** is 4.1–5.8 kcal mol<sup>-1</sup> less. No decoalescence of the methyl peaks or even an increase in the line width was observed when **6** was cooled to –80 °C. Thus, the *ortho* mesityl methyls of the carbamate compound remain chemically equivalent at all temperatures observed. The barrier of rotation in **6** must therefore be smaller than in compounds **7–10**.

A pertinent question is, Does the Ni–Mes or Ni–X group rotate rapidly at elevated temperatures? Given the small variation in the electronic properties of the X group, it is unlikely that these changes will cause a 5 kcal mol<sup>-1</sup> difference in  $\Delta G^\ddagger_{\text{rot}}$  of the Ni–Mes group. There is essentially no difference in the P–Ni–P angles in **8** and **10**; thus changes in the steric properties of the X group would not be expected to affect the  $\Delta G^\ddagger_{\text{rot}}$  of the Ni–Mes group. We conclude that the observed fluxionality in compounds **7–10** arises from hindered rotation of the Ni–X bond. This conclusion is in agreement with the studies of Wada

**Table 4.** Fractional Coordinates and Equivalent Isotropic<sup>a</sup> Thermal Parameters (Å<sup>2</sup>) for the Non-H Atoms of Compound **8**

atom	x	y	z	U
Ni	0.18134(5)	0.14492(2)	0.17765(3)	0.0386(2)
P1	–0.00979(13)	0.08187(6)	0.17955(7)	0.0552(4)
P2	0.38456(12)	0.20059(6)	0.17489(6)	0.0501(4)
O13	0.0664(3)	0.23488(14)	0.0656(2)	0.0584(13)
N	0.0688(3)	0.2290(2)	0.1845(2)	0.0395(11)
C1	0.2881(4)	0.0638(2)	0.1667(2)	0.0435(14)
C2	0.2905(5)	0.0398(2)	0.0964(2)	0.056(2)
C2'	0.1948(6)	0.0731(3)	0.0291(2)	0.073(2)
C3	0.3764(6)	–0.0159(3)	0.0872(3)	0.067(2)
C4	0.4599(6)	–0.0506(3)	0.1464(3)	0.073(2)
C4'	0.5535(7)	–0.1102(3)	0.1349(3)	0.110(3)
C5	0.4534(6)	–0.0286(2)	0.2152(3)	0.065(2)
C6	0.3696(5)	0.0270(2)	0.2269(2)	0.050(2)
C6'	0.3608(5)	0.0457(2)	0.3032(2)	0.063(2)
C7	0.0384(4)	0.2541(2)	0.2503(2)	0.0410(15)
C8	–0.0946(5)	0.2811(2)	0.2557(2)	0.048(2)
C9	–0.1185(7)	0.3041(3)	0.3220(3)	0.066(2)
C10	–0.0091(8)	0.2985(3)	0.3842(3)	0.076(3)
C11	0.1204(8)	0.2690(3)	0.3804(3)	0.074(3)
C12	0.1460(6)	0.2474(3)	0.3147(2)	0.058(2)
C13	0.0360(4)	0.2616(2)	0.1202(2)	0.0428(14)
C14	–0.0312(5)	0.3336(2)	0.1124(2)	0.044(2)
C15	–0.1901(5)	0.3338(2)	0.0701(2)	0.049(2)
C16	–0.2906(6)	0.3755(3)	0.0925(3)	0.060(2)
C17	–0.4338(7)	0.3808(3)	0.0536(4)	0.079(2)
C18	–0.4793(7)	0.3438(4)	–0.0084(4)	0.088(3)
C19	–0.3834(8)	0.3015(4)	–0.0314(4)	0.090(3)
C20	–0.2386(6)	0.2956(3)	0.0076(3)	0.068(2)
C21	0.0598(5)	0.3842(2)	0.0799(2)	0.052(2)
C22	0.0736(6)	0.3805(3)	0.0085(3)	0.071(2)
C23	0.1560(7)	0.4291(5)	–0.0179(4)	0.094(3)
C24	0.2214(8)	0.4806(4)	0.0249(6)	0.101(3)
C25	0.2103(7)	0.4848(3)	0.0951(6)	0.094(3)
C26	0.1283(6)	0.4372(3)	0.1228(3)	0.069(2)
C27	0.5416(5)	0.1801(3)	0.2465(3)	0.102(2)
C28	0.4576(6)	0.1897(3)	0.0947(3)	0.090(3)
C29	0.3815(5)	0.2926(2)	0.1814(3)	0.077(2)
C30	–0.0003(6)	–0.0105(2)	0.1721(3)	0.077(2)
C31	–0.0848(6)	0.0908(3)	0.2599(3)	0.081(2)
C32	–0.1636(6)	0.1034(3)	0.1060(3)	0.097(2)

<sup>a</sup> For anisotropic atoms, the  $U$  value is  $U_{\text{eq}}$ , calculated as  $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$  where  $A_{ij}$  is the dot product of the  $i$ th and  $j$ th direct space unit cell vectors.

**Table 5.** Selected Bond Lengths (Å) and Angles (deg) for the Non-H Atoms of Compound **8**

1	2	3	1–2	1–2–3
P1	Ni	P2	2.183(1)	175.17(6)
P1	Ni	N		90.94(10)
P2	Ni	N	2.206(1)	93.90(10)
P2	Ni	C1		86.03(12)
N	Ni	C1	1.974(3)	177.6(2)
C1	Ni	P1	1.912(4)	89.14(12)
C13	O13		1.241(5)	
C7	N	C13	1.419(5)	124.8(3)
C7	N	Ni		124.1(2)
C13	N	Ni	1.339(5)	110.8(3)
C2	C1	C6	1.407(6)	117.4(4)
C14	C13	O13	1.537(6)	118.3(3)
C14	C13	N		121.9(4)
O13	C13	N		119.7(4)

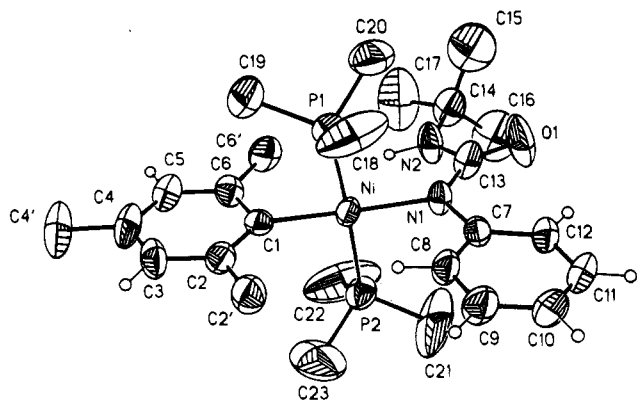
*et al.*, who have examined hindered rotation of the Ni–L group in compounds of the type *trans*-[Ni(PR<sub>3</sub>)<sub>2</sub>(R)(L)]<sup>+</sup> (R = mesityl).<sup>16</sup>

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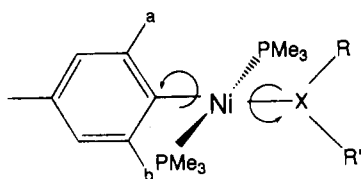
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**Figure 5.** Thermal ellipsoid plot of *trans*-Ni(Mes)[N(Ph)C(O)N(H)CMe<sub>3</sub>](PMe<sub>3</sub>)<sub>2</sub>, **10**. Selected bond lengths, Å: Ni–N1, 1.978(6); Ni–C1, 1.930(7); Ni–P1, 2.212(3); Ni–P2, 2.206(3); N1–C7, 1.411(10); C13–O1, 1.220(12); N2–C13, 1.379(11); N2–C14, 1.475(12). Selected bond angles, deg: P1–Ni–P2, 176.84(12); N1–Ni–C1, 178.0(3); Ni–N1–C7, 118.8(5); C7–N1–C13, 119.8(7); C13–N2–C14, 124.3(8).



**Figure 6.** Hindered rotation in *trans*-(PMe<sub>3</sub>)<sub>2</sub>Ni–mesityl complexes.

**Table 6.** Rotational Barriers for Compounds with Hindered Rotation

compd	$T_c$ , K	$\delta\nu$ , Hz	$\Delta G^\ddagger$ , kcal·mol <sup>-1</sup>
<b>7</b>	348(1)	21(2)	17.8(5)
<b>8</b>	263(2)	155(2)	12.3(5)
<b>9</b>	306(2)	12(2)	16.4(5)
<b>10<sup>a</sup></b>	366(2)	54(2)	18.1(5)

<sup>a</sup>  $T_c$  and  $\delta\nu$  obtained from *meta* mesityl proton resonances.

The similarity in the electronic properties of the X group would not be expected to result in the observed differences in the  $\Delta G^\ddagger_{\text{rot}}$  of the X group. Thus, it is the differences in the steric and conformational properties of the X group that give rise to the variation of  $\Delta G^\ddagger_{\text{rot}}$ . The X-ray structures of **8** and **10** have two very different confirmations of the amide and urea groups, respectively. In **8**, the carbonyl group is oriented over the coordination plane of the Ni atom, while in **10**, the more bulky NH(*t*-Bu) group is oriented over the Ni atom with a rather short Ni–H distance of 2.19 Å. Given the similarity of compounds **9** and **10**, we believe that **9** has the same orientation. Though the X-ray structure of **7** has not been solved, the NOE experiments indicate a *Z* disposition of the Ni and N(H)Ph groups on the C=C bond. This also places the bulky N(H)Ph group over the Ni coordination plane. Thus, it appears that the large barriers to rotation associated with the Ni–X bond that are observed in compounds **7**, **9**, and **10** arise from steric interactions caused by orientation of the bulky N(H)R group toward the metal center. When the carbonyl O atom points toward the metal center, as is observed in **8**, a considerably lower barrier is observed as is expected, given the reduced steric demands of this group. The explanation for why the bulky N(H)R groups in compounds **9** and **10** are oriented over the coordination plane is unclear, but an interaction between the NH proton and the metal center is one possibility.

## Experimental Section

**Materials and Experimental Methods.** All syntheses were carried out under dry argon atmosphere using standard Schlenk techniques.

Mesitylmagnesium bromide, PhNCO, *t*-BuNCO, and CH<sub>3</sub>O<sub>2</sub>CC≡CCO<sub>2</sub>-CH<sub>3</sub> (DMAD) were used as purchased from Aldrich. NiBr(Mes)-(PMe<sub>3</sub>)<sub>2</sub>,<sup>17</sup> NiBr(Ph)(PMe<sub>3</sub>)<sub>2</sub>,<sup>17</sup> and Ph<sub>2</sub>CCO<sup>18</sup> were prepared using literature methods. Tetrahydrofuran (THF), diethyl ether (Et<sub>2</sub>O), and pentane were distilled from sodium benzophenone ketyl. Benzene was distilled from sodium. CO<sub>2</sub> gas was passed through a CaCl<sub>2</sub> drying tube. NMR solvents (C<sub>6</sub>D<sub>6</sub> and CD<sub>2</sub>Cl<sub>2</sub>) were stored over molecular sieves and degassed prior to use. NMR spectra were acquired on either a General Electric QE-300 or a Varian VXR 300 spectrometer. <sup>1</sup>H and <sup>13</sup>C chemical shifts are referenced to deuterated solvents and are reported relative to TMS. <sup>31</sup>P chemical shifts are reported relative to H<sub>3</sub>PO<sub>4</sub>. Elemental analyses were performed by Atlantic Microlabs, Inc., or the analytical services of this department.

**Preparation of *trans*-Ni(Ph)(NHPh)(PMe<sub>3</sub>)<sub>2</sub> (**1a**).** *trans*-NiBr(Ph)-(PMe<sub>3</sub>)<sub>2</sub> (0.27 g, 0.72 mmol) was dissolved in 15 mL of THF, and the mixture was cooled to –78 °C. To this solution was added an excess of KNHPh (0.14 g, 1.07 mmol) in 25 mL of THF. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Solvent was removed under reduced pressure. The solid was extracted with pentane (4 × 20 mL) and concentrated to 25 mL under reduced pressure. Cooling to –10 °C yielded several crops of yellow crystalline product (190 mg). Crystals were dissolved in 25 mL of pentane, and an excess of neat PMe<sub>3</sub> (0.1 mL, 1.0 mmol) was added. The solution was then cooled to –10 °C for 48 h to yield red-orange crystals of (**1a**), which were collected and dried under a flow of argon. Analysis was unobtainable due to facile loss of ligand to form the dimer.

**Preparation of [Ni(Ph)(μ-NHPh)(PMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**1b**).** *trans*-NiBr(Ph)-(PMe<sub>3</sub>)<sub>2</sub> (159 mg, 0.42 mmol) was dissolved in 20 mL of THF, and the mixture was cooled to –78 °C. To this solution was added an excess of KNHPh (78 mg, 0.59 mmol) in 20 mL of THF. The reaction mixture was allowed to warm to room temperature upon addition. After 2 h, solvent was removed under reduced pressure and the oily residue was extracted once with 25 mL of Et<sub>2</sub>O. The orange solution was concentrated to 10 mL and cooled to –10 °C to afford several crops of yellow crystals which were a mixture of **1a** and **1b**. This mixture was heated in an oil bath at 70 °C under reduced pressure for 24 h. The solid was extracted once with 20 mL of pentane. The solvent was removed under reduced pressure to afford 89 mg of **1b** as a yellow solid; yield 70%. Anal. Calcd for C<sub>30</sub>H<sub>40</sub>N<sub>2</sub>Ni<sub>2</sub>P<sub>2</sub>: C, 59.27; H, 6.63; N, 4.61. Found: C, 58.91; H, 6.31; N, 4.29.

**Preparation of *trans*-Ni(Ph)(NH(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>))(PMe<sub>3</sub>)<sub>2</sub> (**2**).** NiBr(Ph)(PMe<sub>3</sub>)<sub>2</sub> (0.16 g, 0.44 mmol) was dissolved in 10 mL of THF, and the mixture was cooled to –78 °C. To this solution was added an excess of KNH(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (0.14 g, 0.65 mmol) in 25 mL of THF. The reaction mixture was warmed to room temperature and stirred for 12 h. Solvent was removed under reduced pressure, and the solid was extracted with pentane (3 × 10 mL). The solution was concentrated under reduced pressure and cooled to –78 °C to yield several crops of **2** as orange crystals (0.16 g); yield 79%. Anal. Calcd for C<sub>24</sub>H<sub>41</sub>NNiP<sub>2</sub>: C, 62.09; H, 8.90; N, 3.02. Found: C, 61.83; H, 8.71; N, 2.99.

**Preparation of *trans*-Ni(Mes)(NHPh)(PMe<sub>3</sub>)<sub>2</sub> (**3**).** *trans*-NiBr(Mes)(PMe<sub>3</sub>)<sub>2</sub> (1.78 g, 4.35 mmol) and an excess of KNHPh (0.86 g, 6.53 mmol) were dissolved in 35 mL of THF. This solution was immediately cooled to –78 °C for 1 h. The reaction mixture was allowed to warm to room temperature, and stirring was continued for 24 h. Solvent was removed under reduced pressure. The solid was extracted with pentane (3 × 20 mL), and the solution was concentrated under reduced pressure to 25 mL and cooled to –10 °C to yield several crops of **3** as yellow crystals (1.70 g); yield 89%. Anal. Calcd for C<sub>21</sub>H<sub>35</sub>NNiP<sub>2</sub>: C, 59.75; H, 8.36; N, 3.32. Found: C, 59.96; H, 8.39; N, 3.18.

**Preparation of *trans*-Ni(Mes)(NH(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>))(PMe<sub>3</sub>)<sub>2</sub> (**4**).** *trans*-NiBr(Mes)(PMe<sub>3</sub>)<sub>2</sub> (1.20 g, 2.93 mmol) and an excess of KNH(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (0.95 g, 4.40 mmol) were dissolved in 50 mL of THF. This solution was immediately cooled to –78 °C for 2 h. The reaction mixture was allowed to warm to room temperature, and stirring was continued for 24 h. The solvent was removed under reduced pressure.

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The solid was extracted with pentane (4 × 25 mL). The solution was then cooled to -78 °C to yield several crops of **4** as orange-red crystals (1.19 g); yield 80%. Anal. Calcd for C<sub>27</sub>H<sub>47</sub>NNiP<sub>2</sub>: C, 64.04; H, 9.36; N, 2.78. Found: C, 63.81; H, 9.29; N, 2.67.

**Preparation of [Ni(Mes)(μ-OH)(PMe<sub>3</sub>)<sub>2</sub>] (5).** To a solution of *trans*-Ni(Mes)(NH(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(PMe<sub>3</sub>)<sub>2</sub>) (0.15 g, 0.30 mmol) in 15 mL of Et<sub>2</sub>O was added 25 μL of H<sub>2</sub>O (1.39 mmol). The red solution turned yellow within 5 min. After 1 h of stirring, the solution was concentrated to 10 mL under reduced pressure. The solution was cooled to -10 °C to afford **5** as yellow crystals (69 mg); yield 89%. IR: ν<sub>O-H</sub> = 3658 cm<sup>-1</sup>.

**Preparation of *trans*-Ni(Mes)(OC(O)NHPH)(PMe<sub>3</sub>)<sub>2</sub> (6).** CO<sub>2</sub> gas was bubbled into a solution of *trans*-Ni(Mes)(NHPH)(PMe<sub>3</sub>)<sub>2</sub> (0.25 g, 0.59 mmol) in 30 mL of pentane for 5 min. A flocculent yellow solid precipitated. The mixture was cooled to -78 °C to afford **6** as a yellow solid (0.21 g); yield 76%. Anal. Calcd for C<sub>22</sub>H<sub>35</sub>NNiO<sub>2</sub>P<sub>2</sub>: C, 56.68; H, 7.57; N, 3.00. Found: C, 56.73; H, 7.57; N, 3.05.

**Preparation of *trans*-Ni(Mes)[C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)NHPH](PMe<sub>3</sub>)<sub>2</sub> (7).** To a solution of *trans*-Ni(Mes)(NHPH)(PMe<sub>3</sub>)<sub>2</sub> (0.22 g, 0.52 mmol) in 15 mL of pentane was added 1 equiv of CH<sub>3</sub>O<sub>2</sub>CC≡CCO<sub>2</sub>CH<sub>3</sub>, DMAD (0.36 mL, 1.43 M in THF, 0.52 mmol). After 12 h, the solution was cooled to -78 °C to yield several crops of **7** as a yellow solid (0.21 g); yield 71%. Anal. Calcd for C<sub>27</sub>H<sub>41</sub>NNiO<sub>4</sub>P<sub>2</sub>: C, 57.47; H, 7.32; N, 2.48. Found: C, 57.46; H, 7.34; N, 2.48.

**Preparation of *trans*-Ni(Mes)[N(Ph)C(O)CHPh<sub>2</sub>](PMe<sub>3</sub>)<sub>2</sub> (8).** To a solution of *trans*-Ni(Mes)(NHPH)(PMe<sub>3</sub>)<sub>2</sub> (0.20 g, 0.47 mmol) in 25 mL of pentane was added 1 equiv of Ph<sub>2</sub>CCO (0.75 mL, 0.63 M in toluene, 0.47 mmol). After 2 h of stirring, the solution was cooled to -10 °C to yield **8** as orange crystals (0.21 g); yield 73%. Anal. Calcd for C<sub>35</sub>H<sub>45</sub>NNiOP<sub>2</sub>: C, 68.20; H, 7.36; N, 2.27. Found: C, 67.87; H, 7.39; N, 2.18.

**Preparation of *trans*-Ni(Mes)[N(Ph)C(O)N(H)Ph](PMe<sub>3</sub>)<sub>2</sub> (9).** To a solution of *trans*-Ni(Mes)(NHPH)(PMe<sub>3</sub>)<sub>2</sub> (0.20 g, 0.47 mmol) in 20 mL of pentane was added 1 equiv of PhNCO (52 μL, 0.47 mmol). After 12 h of stirring, the solution was cooled to -10 °C to afford **9** as a yellow-orange solid (205 mg); yield 80%. Calcd for C<sub>28</sub>H<sub>40</sub>N<sub>2</sub>-NiOP<sub>2</sub>: C, 62.13; H, 7.45; N, 5.17. Found: C, 62.08; H, 7.45; N, 5.15.

**Preparation of *trans*-Ni(Mes)[N(Ph)C(O)N(H)CMe<sub>3</sub>](PMe<sub>3</sub>)<sub>2</sub> (10).** To a solution of *trans*-Ni(Mes)(NHPH)(PMe<sub>3</sub>)<sub>2</sub> (0.14 g, 0.32 mmol) in 15 mL of benzene was added 1 equiv of (CH<sub>3</sub>)<sub>3</sub>CNCO (37 μL, 0.32 mmol). After 12 h of stirring, the solvent was removed under reduced pressure. The solid was dissolved in 20 mL of pentane, and the solution was concentrated to ca. 5 mL under reduced pressure. Cooling to -10

°C afforded **10** as bright yellow crystals (124 mg); yield 75%. Calcd for C<sub>26</sub>H<sub>44</sub>N<sub>2</sub>NiOP<sub>2</sub>: C, 59.91; H, 8.51; N, 5.37. Found: C, 59.92; H, 8.52; N, 5.39.

**X-ray Experimental Details.** Data were collected at room temperature on a Siemens P3m/V diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation (λ = 0.710 73 Å). Thirty-two reflections with 20.0° ≤ 2θ ≤ 22.0° were used to refine the cell parameters. Four reflections were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on *I* was 3%). Absorption corrections were applied on the basis of measured crystal faces using SHELXTL Plus.<sup>19</sup> The structure was solved by the heavy-atom method in SHELXTL Plus from which the location of the Ni atom was obtained. The rest of the non-hydrogen atoms were obtained from subsequent difference Fourier maps. The structure was refined in SHELXTL Plus using full-matrix least squares, and all of the non-H atoms were refined anisotropically. The positions of the non-methyl H atoms were obtained from difference Fourier maps and refined without any constraints. The methyl H atoms were calculated in ideal positions, and their isotropic thermal parameters were fixed. The linear absorption coefficients were calculated from values from ref 20. Scattering factors for non-hydrogen atoms were taken from Cromer and Mann<sup>21</sup> with anomalous-dispersion corrections from Cromer and Liberman,<sup>22</sup> while those of hydrogen atoms were from Stewart, Davidson, and Simpson.<sup>23</sup>

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**Supporting Information Available:** A table of <sup>13</sup>C NMR data for all compounds and tables of crystallographic data, hydrogen positional parameters, bond lengths and angles, and anisotropic thermal parameters for **8** (10 pages). Ordering information is given on any current masthead page.

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