constants with an estimated 10% error and temperatures (±1 °C) could be correlated at a confidence level greater than 99% with use of the Eyring and Arrhenius equations.

For the carbonyl group scrambling process, the free energy of activation at the coalescence temperature, $\Delta G^{\ddagger}{}_{T_c}$, was also calculated by using the approximate expressions applicable to the two-site exchange problem.[35]

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η^1- and η^2-Alkaneimidoyl Complexes of Nickel: Synthesis and Properties

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The insertion of CNBu^t into the Ni–C bond of the alkyls *trans*-Ni(R)Cl(PMe$_3$)$_2$ gives the η^1-alkaneimidoyls Ni[η^1-C(NBu^t)R]Cl(PMe$_3$)$_2$ (R = CH$_3$ (**1**), CH$_2$CMe$_2$Ph (**2**)), but for R = CH$_2$SiMe$_3$ and CH$_2$CMe$_3$, both η^1 and η^2 species can be isolated, Ni[η^1-C(NBu^t)R]Cl(PMe$_3$)$_2$ (R = CH$_2$SiMe$_3$ (**3**), CH$_2$CMe$_3$ (**4**)), Ni[η^2-C(NBu^t)R]Cl(PMe$_3$) (R = CH$_2$SiMe$_3$ (**5**), CH$_2$CMe$_3$ (**6**)). Facile η^1–η^2 interconversions can be achieved; addition of PMe$_3$ to solutions of **5** or **6** produces **3** or **4**, respectively, while PMe$_3$ removal from the η^1 compounds affords the corresponding η^2-alkaneimidoyls. The analogous insertion of CNBu^t into the Ni–C bond of the alkyl-pyrrolyls Ni(R)(NC$_4$H$_2$X$_2$)(PMe$_3$)$_2$ affords only η^2-alkaneimidoyl structures, Ni[η^2-C(NBu^t)R](NC$_4$H$_2$X$_2$)(PMe$_3$) (X = H, R = Me (**7**); X = Me, R = Me (**8**), CH$_2$SiMe$_3$ (**9**), CH$_2$CMe$_3$ (**10**)). On the other hand, the 18-electron η^1-alkaneimidoyls CpNi[η^1-C(NBu^t)R]PMe$_3$ (R = Me (**11**), CH$_2$CMe$_2$Ph (**12**)) can be obtained by the reaction of NaCp with **1** and **2** respectively, while the interaction of **1** with NaS$_2$CNMe$_2$ yields Ni[η^1-C(NBu^t)Me](S$_2$CNMe$_2$)PMe$_3$ (**13**). The η^1-alkaneimidoyls also undergo facile protonation to the corresponding cationic aminocarbene complexes, e.g., [Ni(C(NHBu^t)Me)Cl(PMe$_3$)$_2$]Cl (**14a**). All the η^1-alkaneimidoyls display ν(C=N) in the range 1630–1590 cm^{-1}, while for the η^2-alkaneimidoyls a shorter and higher frequency range is observed (1730–1710 cm^{-1}). In the η^1-alkaneimidoyls, the nickel-bound carbon atom resonates at ca. 190–185 ppm (with the exception of the 18-electron complexes **11** and **12**, for which δ(Ni–*C*) $\simeq$ 177 ppm), while in the η^2-alkaneimidoyls this resonance appears at ca. 170 ppm.

The migratory insertion of isocyanides, CNR, into transition metal–carbon bonds is a commonly observed reaction that has received considerable attention in recent years, due in part to its similarity to the analogous, and technically more important, carbon monoxide insertion. Both η^1- and η^2-alkaneimidoyl functionalities[1] can in principle be obtained. The lanthanides, actinides, and the early transition metals (groups 3d to 5d) frequently yield η^2 structures,[2–4] possibly as a reflection of the high affinity that these elements exhibit toward nitrogen. Conversely, the softer later transition metals (groups 8d to 10d) provide mainly η^1 structures, and in fact there seems to be no fully characterized η^2-alkaneimidoyl (or acyl) complexes of the elements to the right of the iron triad.[1a] η^2-Alkaneimidoyl complexes of Fe and Ru and Co have been reported,[5] and bridging η^2-alkaneimidoyl structures have recently been ascertained,[6] but to our knowledge no mononuclear η^2-alkaneimidoyl complexes are presently known for the elements of the nickel triad. Furthermore, while the single and the multiple insertions of isocyanides into Pd–C and Pt–C bonds have been intensively studied,[7,8] information on the analogous nickel systems is more restricted.[9,10]

With the above considerations in mind and as a natural extension of our earlier work on the insertion of CO into nickel–carbon bonds,[11] we have undertaken an investiga-

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Table I. Analytical, IR, and ^1H NMR Data for Alkaneimidoyl Complexes

	anal. data[a]		IR $\nu(C{=}N)$,[b]	^1H NMR, δ (J, Hz)[c]		
	C	H	cm^{-1}	PMe_3[d]	Bu^t	others
1	42.0 (41.8)	8.6 (8.7)	1620, 1590	1.04 (br s)	1.68	2.15 (br s, Me)
2	54.0 (54.5)	8.6 (8.6)	1620, 1600	1.00 (t, 3.5)	1.56	1.59 (CMe_2); 2.91 (CH_2); 7.0–7.5 (C_6H_5)
3	43.5 (43.2)	9.3 (9.1)	1590	1.05 (t, 3.4)	1.59	0.18 ($SiMe_3$); 2.01 (CH_2)
4			1635, 1595	1.13 (t, 3.2)	1.61	1.14 (CMe_3); 2.51 (CH_2)
5	42.1 (42.3)	8.6 (8.5)[e]	1720	1.02 (d, 8.4)	1.27	−0.08 ($SiMe_3$); 1.75 (CH_2)
6			1730	1.05 (d, 8.3)	1.30	0.78 (CMe_3); 2.08 (CH_2)
7			1720	0.76 (d, 8.6)	1.00	1.54 (Me); 6.94, 7.18 (CH, pyrr)
8	55.3 (55.1)	8.8 (8.8)[f]	1720	0.76 (d, 8.5)	0.98	1.53 (Me); 2.91, 6.50 (Me, CH, pyrr)
9	53.8 (54.2)	9.2 (9.2)	1710	0.82 (d, 7.9)	1.05	−0.01 ($SiMe_3$); 1.89 (CH_2); 2.90, 6.47 (Me, CH, pyrr)
10	59.5 (59.6)	9.7 (9.7)[g,h]	1715	0.78 (d, 8.1)	1.05	0.82 (CMe_3); 2.06 (CH_2); 2.91, 6.51 (Me, CH, pyrr)
11			1620, 1590	0.72 (d, 8.8)	1.57	2.40 (Me); 5.14 (C_5H_5)
12	66.2 (66.4)	8.8 (8.7)	1635	0.71 (d, 8.8)	1.31	1.46, 1.56 (CMe_2); 2.71, 3.45 (CH_2, d, 17.3); 5.12 (C_5H_5); 7.0–7.5 (C_6H_5)
13	40.7 (40.8)	7.7 (7.6)	1620, 1590[i]	0.87 (d, 8.2)	1.96	2.53 (CMe); 2.54, 2.56 (NMe_2)

[a] Calculated values in parentheses. [b] Nujol mull. [c] C_6D_6, singlets unless otherwise indicated. [d] Apparent or real J_{HP}. [e] M_r(cryoscopic, C_6H_6) = 342 (340). [f] N: 8.1 (8.6). [g] N: 7.2 (7.3). [h] M_r(cryoscopic, C_6H_6) = 386 (383). [i] $\nu_{C{=}N}(S_2CNMe_2)$ = 1535 cm^{-1}.

Table II. $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR Data for Alkaneimidoyl Complexes[a]

		$^{13}C\{^1H\}$, δ (J, Hz)				
	$^{31}P\{^1H\}$, δ	PMe_3[b]	Ni–C	$C\mathit{Me}_3$	$\mathit{C}Me_3$	others
1	−16.4	13.9 (t, 13.0)	186.3 (t, 25.0)	31.6	55.7	31.9 (t, 8.0, Me)
2	−18.0	13.7 (t, 13.1)	184.3 (t, 21.8)	30.8	55.8	28.6 (Me_2); 41.5 (CMe_2); 58.2 (t, 7.2, CH_2), 125.2, 126.6, 127.5, 150.8 (aromatics)
3	−17.2	13.7 (t, 13.0)	189.1 (t, 24.3)	31.2	55.7	0.5 ($SiMe_3$); 37.3 (t, 5.7, CH_2)
4	−18.7	14.6 (t, 13.5)	186.4 (t, 22.2)	31.0	56.5	30.3 ($C\mathit{Me}_3$); 33.2 ($\mathit{C}Me_3$); 57.5 (t, 7.7, CH_2)
5	−4.5	15.1 (d, 26.4)	170.0 (d, 13.5)	29.3	*c*	−0.8 ($SiMe_3$); 20.4 (d, 5.8, CH_2)
6	−6.5	15.7 (d, 27.0)	169.3 (d, 12.7)	29.3	59.1 (d, 4.2)	30.0 ($C\mathit{Me}_3$); 31.6 ($\mathit{C}Me_3$); 40.6 (d, 4.7, CH_2)
7	−1.6	14.9 (d, 26.1)	*c*	29.1	*c*	14.2 (d, 5.7, Me)
8	−0.7	15.1 (d, 25.4)	170.8 (d, 15.7)	28.8	56.1 (d, 6.0)	14.1 (d, 6.3, Me); 18.2 (Me, pyrr); 106.1, 132.4 (CH, *C*Me, pyrr)
9	−2.8	15.2 (d, 24.8)	169.3 (d, 13.9)	29.2	55.9 (d, 5.6)	−0.5 ($SiMe_3$); 18.3 (Me, pyrr); 21.0 (d, 5.2, CH_2); 106.2, 132.3 (CH, *C*Me, pyrr)
10	−4.0	15.0 (d, 24.7)	172.6 (d, 13.5)	29.2	57.0 (d, 5.6)	18.3 (Me, pyrr); 30.0 ($C\mathit{Me}_3$); 31.2 ($\mathit{C}Me_3$); 41.1 (d, 4.1, CH_2); 106.5, 132.2 (CH, *C*Me, pyrr)
11	−8.2	18.7 (d, 27.8)	178.2 (d, 22.0)	30.7	54.9	40.8 (d, 8.0, Me); 90.4 (C_5H_5)
12	−4.2	18.6 (d, 27.8)	176.5 (d, 22.2)	29.9	55.0	28.6, 30.9 (Me_2); 39.7 ($\mathit{C}Me_2$); 66.8 (d, 6.4, CH_2); 90.7 (C_5H_5); 124.4, 126.0, 127.5, 151.4 (aromatics)
13	−5.7	14.5 (d, 26.0)	189.1 (d, 24.0)	32.1	56.3	31.5 (d, 7.6, Me); 37.6, 38.5 ($N\mathit{Me}_2$); 208.9 (br s, $\mathit{C}NMe_2$)

[a] C_6D_6, singlets unless otherwise indicated. [b] Apparent or real J_{CP}. [c] No resonances observed.

Table III. Analytical, IR, and ^1H NMR Data for Cationic Carbene Complexes

	anal. data[a]		IR $\nu(C{=}N)$,[b]	^1H NMR, δ (J, Hz)[c]			
	C	H	cm^{-1}	PMe_3[d]	Bu^t	NH	others
14b	32.5 (33.3)	7.2 (7.2)	1570	1.36 (t, 4.2)	1.83	12.5 (br)	2.73 (br t, 1.5, Me)
15			1565	1.46 (t, 4.1)	1.84	8.9 (br)	1.14 (CMe_3); 2.95 (br s, CH_2)
17	54.0 (54.8)	7.3 (7.3)	1560	1.32 (d, 10.3)	1.17	8.4 (br)	1.40 (br, CMe_2); 3.28, 3.77 (d, 17.7, CH_2); 5.32 (C_5H_5); 7.2–7.5 (C_6H_5)
18	32.7 (32.7)	6.3 (6.3)	1580[e]	1.32 (d, 9.6)	1.82	9.6 (br)	2.62 (br, Me); 3.22, 3.23 (NMe_2)

[a] Calculated values in parentheses. [b] Nujol mull. [c] CD_2Cl_2, singlets unless otherwise indicated. [d] Apparent or real J_{HP}. [e] $\nu C{=}N(S_2CNMe_2)$ = 1550 cm^{-1}.

tion of the analogous isocyanide insertion reaction. It soon became evident that, at variance with the results found for the CO insertion, both η^1 and η^2 structures can be obtained. Therefore this study, whose results are herein reported, has allowed characterization of the first η^2-alkaneimidoyl complexes of nickel. Furthermore, interconversion of the η^1- and η^2-metal–alkaneimidoyl linkages can be readily achieved. Although the $\eta^2 \rightarrow \eta^1$ transformation has been observed previously in transition metal–acyl complexes,[12] it is, to our knowledge unprecedented in alkaneimidoyl chemistry. During the progress of this work some of the complexes described have been independently reported.[13]

Results and Discussion

Diethyl ether solutions of the chloroalkyl derivatives $Ni(R)Cl(PMe_3)_2$ ($R = CH_3, CH_2CMe_2Ph$) react with 1 equiv of $CNBu^t$ with formation of crystalline red **1** and yellow **2**, respectively, in good yields. Analytical data reveal **1** and **2** have incorporated one molecule of the isocyanide per molecule of the original nickel–alkyl, while IR and NMR studies (Tables I and II) clearly show the reaction occurs with $CNBu^t$ insertion into the Ni–C bond as depicted in eq 1. Thus, their IR spectra display, in addition

$$\mathit{trans}\text{-}Ni(R)Cl(PMe_3)_2 + CNBu^t \rightarrow \mathit{trans}\text{-}Ni[C(NBu^t)R]Cl(PMe_3)_2 \quad (1)$$
$$R = CH_3,\ \mathbf{1};\ CH_2CMe_2Ph,\ \mathbf{2}$$

to bands due to the PMe_3 ligands, a medium absorption around 1600 cm^{-1}, suggesting the formation of an alkaneimidoyl ligand. In some of these and other alkane-

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Table IV. $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR Data for Cationic Carbene Complexes[a]

		$^{13}C\{^1H\}$, δ (J, Hz)				
	$^{31}P\{^1H\}$, δ	PMe_3[b]	Ni–C	C*Me*$_3$	CMe_3	others
14b	−11.9	13.4 (t, 15.5)	235.6 (t, 30.7)	29.4	58.9	31.7 (Me)
15	−13.5	14.4 (t, 16.5)	246.1 (t, 28.2)	28.9	60.9	30.5 (C*Me*$_3$); 31.8 (CMe_3); 58.0 (CH_2)
17	−4.5	18.2 (d, 32.3)	244.7 (d, 25.2)	28.7	59.0	28.3, 31.5 (C*Me*$_2$); 39.1 (CMe_2); 64.4 (CH_2); 94.1 (C_5H_5); 126.0, 127.8, 130.1, 140.6 (aromatics)
18	−5.8	13.6 (d, 30.8)	246.4 (d, 27.4)	29.3	59.5	32.9 (Me); 38.4, 38.7 (NMe_2); 204.2 (d, 3.9, $CNMe_2$)

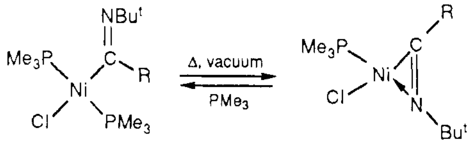
[a] CD_2Cl_2, singlets unless otherwise indicated. [b] Apparent or real J_{CP}.

imidoyl compounds described in this work, two ν(C=N) bands are sometimes observed, due possibly to crystal packing effects. Although the value of ν(C=N) seems to be a rather inconsistent parameter for the assignment of the alkaneimidoyl bonding mode (see below), the low frequency of this band for **1** and **2** suggests η^1 coordination. This is in accord with the high tendency of nickel to adopt a 16-electron configuration in complexes of this type, and it is also in agreement with the structure proposed by Bochmann and co-workers for compound **1** in their independent report of alkaneimidoyl complexes of nickel.[13] ^1H, ^{13}C, and ^{31}P NMR data are also in accord with the proposed formulation. In particular we note that the NiC(NBu^t)R resonance appears as a triplet, centered at ca. 185 ppm, due to coupling to the two equivalent ^{31}P nuclei.

The analogous reaction of CNBu^t (1 equiv) with the (trimethylsilyl)methyl and the neopentyl derivatives, $Ni(R)Cl(PMe_3)_2$, takes a rather unexpected course since it furnishes two kind of products that can be easily separated by fractional crystallization. Compounds **3** and **4** have analytical composition $Ni[C(NBu^t)R]Cl(PMe_3)_2$ (R = CH_2SiMe_3; **3**; CH_2CMe_3, **4**) and display spectroscopic properties very similar to those described above for **1** and **2**. They are therefore formulated as η^1-alkaneimidoyl complexes, $Ni[\eta^1\text{-}C(NBu^t)R]Cl(PMe_3)_2$. The other type of complex has analytical composition $Ni[C(NBu^t)R]Cl(PMe_3)$ (R = CH_2SiMe_3, **5**; CH_2CMe_3, **6**). The monomeric nature of these species, demonstrated by cryoscopic molecular weight measurements carried out in C_6H_6, rules out possible dimeric formulations and suggests that the 16-electron configuration at the nickel center is achieved by virtue of a η^2 interaction with the alkaneimidoyl ligand. In accord with this, their IR spectra display ν(C=N) at ca. 1730–1720 cm^{-1}, i.e., there is a shift of more than 100 cm^{-1} to higher frequency with respect to the corresponding η^1-alkaneimidoyl. This is at variance with the behavior found for η^1- and η^2-acyl structures for which the η^2 coordination is characterized by lower ν(C=O) values[1,14] but is in agreement with the results reported for η^1- and η^2-alkaneimidoyl complexes of molybdenum,[15] for which the $\eta^1 \rightarrow \eta^2$ change in the bonding mode is accompanied by an increase in the C–N bond order, manifested in a concomitant increase of the C=N stretching frequency. Thus for the η^1-alkaneimidoyl $CpMo[\eta^1\text{-}C(NC_6H_5)Me](CO)_2[P(OMe)_3]$, ν(C=N) appears at the low frequency of 1570 cm^{-1}, while the related η^2-alkaneimidoyls $CpMo[\eta^2\text{-}C(NR)Me](CO)_2$ (R = Me, C_6H_5) absorb at ca. 1700 cm^{-1}. It seems therefore that for the η^2-alkaneimidoyl structures the C=N stretching vibration appears at higher frequencies than for the corresponding η^1-alkaneimidoyls.

As can be seen from data in Tables I and II, ^1H and ^{13}C NMR studies are in accord with the η^2 formulation proposed for **5** and **6**. The nickel-bound alkaneimidoyl carbon atom resonates at ca. 170 ppm and appears as a doublet ($^2J_{CP}$ = 13 Hz) as a result of its coupling to the ^{31}P nucleus. The magnitude of this coupling indicates a cis distribution of the alkaneimidoyl carbon and the ^{31}P nucleus. In related square-planar complexes of nickel, cis $^2J_{CP}$ are of the order[16] of 10–25 Hz, while trans couplings have higher values (50–80 Hz).

The η^1-alkaneimidoyls **3** and **4** and the corresponding η^2 derivatives **5** and **6** can be readily interchanged. Addition of PMe_3 to solutions of **5** and **6** provides **3** and **4** in instant, essentially quantitative reactions, while PMe_3 removal by occasional pumping of Et_2O solutions of **3** and **4**, heated at 40 °C, yields the corresponding η^2-alkaneimidoyls (eq 2).



(2)

3, 4 5, 6

R = CH_2SiMe_3, **3**, **5**; CH_2CMe_3, **4**, **6**

An alternative route to effect the η^1–η^2 transformation is by PMe_3 abstraction from **3** or **4** using $Ni(cod)_2$, as indicated in eq 3, but the reaction is not clean and workup of the reaction mixture proves difficult.

$$\underset{\mathbf{3,4}}{2Ni[\eta^1\text{-}C(NBu^t)R]Cl(PMe_3)_2} + Ni(cod)_2 \rightarrow \underset{\mathbf{5,6}}{2Ni[\eta^2\text{-}C(NBu^t)R]Cl(PMe_3)} + Ni(cod)(PMe_3)_2 + cod \qquad (3)$$

We have described recently the formation of pyrrolyl–organometallic complexes of nickel of composition $Ni(R)(NC_4H_2X_2)(PMe_3)_2$, for various combinations X = H, Me; R = Me, CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph and 2,4,6-$C_6H_2Me_3$, and studied their carbonylation.[17] Observation of the reductive elimination products, $Ni(CO)_2(PMe_3)_2$ and $RC(O)NC_4H_2X_2$, was ascribed to the well-known propensity of CO to induce reductive elimination[18] in the corresponding acyls "$Ni(COR)(NC_4H_2X_2)(PMe_3)_2$". We considered it of interest to investigate the analogous isocyanide insertion, and with this aim in mind the reaction of CNBu^t and the pyrrolyls $Ni(R)(NC_4H_2X_2)(PMe_3)_2$ has been pursued. As shown in eq 4, addition of CNBu^t to solutions of the above pyrrolyls furnish the yellow-to-red microcrystalline complexes **7–10**. ^{31}P NMR studies indicate the reaction proceeds with liberation of PMe_3, while analytical and molecular weight determinations demonstrate compounds **7–10** are mono-

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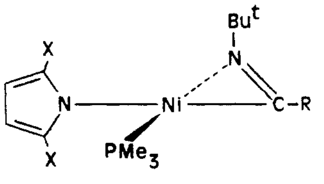
$$\mathrm{Ni(R)(NC_4H_2X_2)(PMe_3)_2 + CNBu^t \rightarrow Ni[\eta^2\text{-}C(NBu^t)R](NC_4H_2X_2)(PMe_3) + PMe_3} \quad (4)$$

7, X = H, R = Me
8, X = Me, R = Me
9, X = Me, R = CH_2SiMe_3
10, X = Me, R = CH_2CMe_3

nuclear complexes that have incorporated one molecule of $CNBu^t$ per molecule of the starting nickel compound.

Spectroscopic data support the proposed η^2 formulation since the alkaneimidoyl ligand gives rise to an IR absorption at 1720–1700 cm^{-1} due to ν(C=N) and to a doublet at ca. 170 ppm ($^2J_{CP}$ = ca. 14 Hz) in the ^{13}C NMR spectrum. The carbon atoms of the pyrrolyl ligands are equivalent two by two (Table II), and this indicates either that there is free rotation around the Ni–N bond or that the pyrrolyl ligand is rigidly in a position perpendicular to the Ni–C–N plane. On the basis of the above and on steric grounds, A seems a reasonable proposal for the solid-state structure of complexes **7**–**10**. Interestingly, the (trimethylsilyl)methyl derivative **9** undergoes a smooth hydrolitic cleavage of the $Me_3Si–CH_2$ bond by water to give the methyl derivative **8** as depicted in eq 5. Similar desilylation reactions have been observed in η^2-acyl complexes[14] as well as in other systems.[19,20]



A

$$\underset{\mathbf{9}}{\mathrm{Ni[\eta^2\text{-}C(NBu^t)CH_2SiMe_3](NC_4H_2Me_2)(PMe_3)}} \xrightarrow{H_2O} \underset{\mathbf{8}}{\mathrm{Ni[\eta^2\text{-}C(NBu^t)CH_3](NC_4H_2Me_2)(PMe_3)}} \quad (5)$$

Before closing this section, some comments will be devoted to the structural characterization of η^1- and η^2-alkaneimidoyl functionalities by spectroscopic means. Both the value of ν(C=N) and the position of the ^{13}C NMR resonance of the alkaneimidoyl carbon have been used for the assignment of the alkaneimidoyl bonding mode. ν(C=N) for η^2 structures encompasses a very wide frequency range which includes that accepted for η^1-alkaneimidoyls. Neutral η^2-alkaneimidoyls of the lanthanides, actinides, and the groups 3d–5d metals consistently have ν(C=N) IR bands below 1600 cm^{-1}, but the cationic species $[Cp_2Ti(\eta^2\text{-}C(NBu^t)Me)(CNBu^t)]^+$, structurally characterized as the MeCN solvate of the BPh_4^- salt,[21] displays this absorption at 1740 cm^{-1}. Neutral η^2-alkaneimidoyl complexes of molybdenum[15] and ruthenium[5a] have ν(C=N) at 1720–1650 cm^{-1}, and the cations $[Fe(\eta^2\text{-}C(NBu^t)Me)(CO)_2(PMe_3)_2]^+$ [5b] and $[CpCo(\eta^2\text{-}C(NBu^t)Me)(PMe_3)]^+$ [5c] display this band at the even higher frequencies of 1750 and 1780 cm^{-1}, respectively. Therefore for neutral η^2-alkaneimidoyls ν(C=N) bands in the range 1490[2] to 1720[15] cm^{-1} have been reported, and this obviously includes the frequency range 1650–1550 cm^{-1} found for M–η^1-C(NR)R′ derivatives (e.g., 1570 cm^{-1}, M = Mo;[15] 1620–1550 cm^{-1}, M = Ni,[13] Pd;[7a,b,8b,c] 1590 cm^{-1}, M = Pt;[22] etc). A possible exception to this range for η^1-alkaneimidoyls could be the 1720-cm^{-1} value reported for **3** by Bochmann and coworkers.[13] However, the coincidence of this value with that found in this work for the analogous η^2-alkaneimidoyl **5** suggests that the formation of the latter complex may have been overlooked in the work reported in ref 13.

The situation is therefore rather confusing, although as already indicated, it seems that whenever the two types of complexes are known for the same element (Mo, ref 15; Ni, this work), ν(C=N) for the η^2 compounds is higher than for the η^1 analogues. But in general, the value of ν(C=N) is a rather inconsistent parameter for the assignment of the bonding mode of the alkaneimidoyl ligand.[10,21]

The range 195–270 ppm has been found for the ^{13}C NMR resonance of the metal-bound η^2-alkaneimidoyl carbon.[1a,2,21] It should be noted however that this range corresponds to compounds of the lanthanides, actinides, and the early transition metals up to the group 6d metals and that information on the analogous complexes of the middle and the late transition metals is virtually nonexistent. For the η^2-alkaneimidoyls of Ni(II) described in this work the $\overline{\mathrm{Ni–C}}$(NR)R′ resonance is shifted to higher field (ca. 170 ppm). On the other hand, the 16-electron η^1-alkaneimidoyls **1**–**4** consistently give somewhat lower field resonances that are typically in the range 190–185 ppm, but the 18-electron cyclopentadienyl derivatives **11** and **12**, also exhibiting η^1-alkaneimidoyl functionalities (see below), display this signal at 176–178 ppm. It becomes therefore evident that in these compounds the ^{13}C resonance of the alkaneimidoyl group has very little value per se to attest to the bonding mode of this ligand. Finally, it should be mentioned that the shift to higher field observed in going from the η^1- to the η^2-alkaneimidoyl structures is in the direction opposite to that observed for the molybdenum compounds[15] $CpMo[\eta^1\text{-}C(NC_6H_5)Me](CO)_2[P(OMe)_3]$ (155.5 ppm) and $CpMo[\eta^2\text{-}C(NMe)Me](CO)_2$ (202 ppm). At present we cannot offer any reasonable explanation for this different behavior, which clearly points out that general rules to distinguish between η^1- and η^2-alkaneimidoyl functionalities cannot be given.

Some Chemical Reactions of the Alkaneimidoyls 1–4. Scheme I summarizes the reactions investigated. As expected, the η^1-alkaneimidoyls undergo nucleophilic displacement of the chloride ligand by the η^5-cyclopentadienyl group, with formation of the 18-electron species $CpNi[\eta^1\text{-}C(NBu^t)R]PMe_3$ (R = Me, **11**; CH_2CMe_2Ph, **12**). In accord with the proposed η^1 formulation for the alkaneimidoyl ligand, the IR spectra of **11** and **12** show ν(C=N) at 1630–1600 cm^{-1}. The alkaneimidoyl carbon gives rise to a resonance at 176–178 ppm, that is, at a chemical shift intermediate between those of the 16-electron η^1- and η^2-alkaneimidoyl compounds prepared in this work. An analogous reaction is observed between **1** and NaS_2CNMe_2. This provides the 16-electron complex $Ni[\eta^1\text{-}C(NBu^t)Me](S_2CNMe_2)PMe_3$, **13**, for which ν(C=N) and the chemical shift of the alkaneimidoyl carbon are very similar to the corresponding values found for others η^1-alkaneimidoyls of nickel (Tables I and II).

Transition-metal compounds containing a M—C=NR group are readily protonated, even by mild acids. This seems to be a general reaction for alkaneimidoyl complexes and has been widely used to prepare aminocarbene functionalities.[23-25] A remarkable feature of the Ni–η^1-alka-

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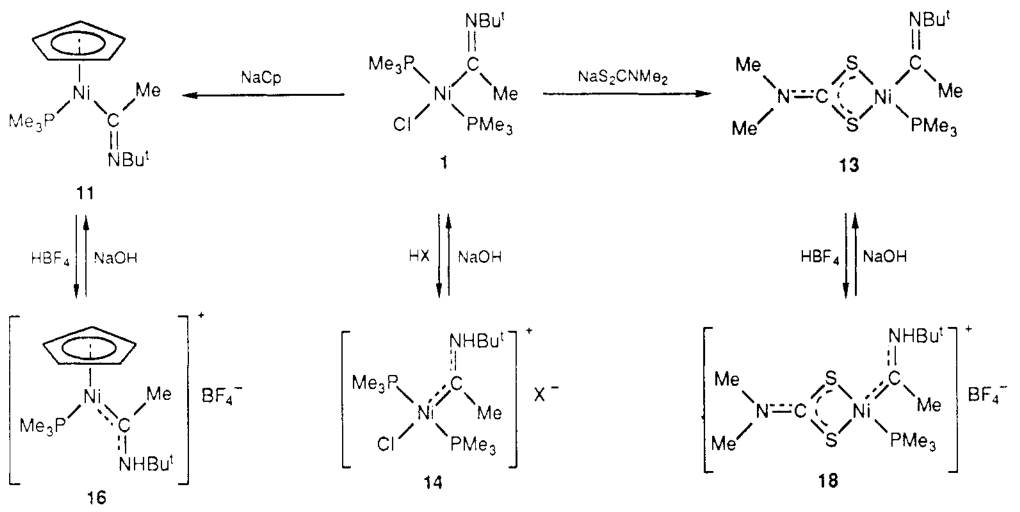
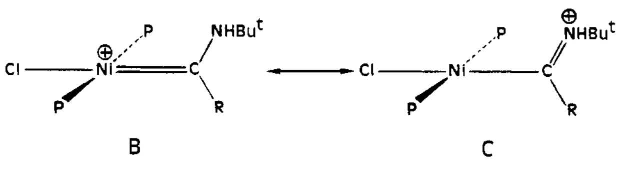
Scheme I



neimidoyl derivatives herein described is the extreme facility with which they can be protonated (Scheme I). Indeed, addition of a few drops of water to solutions of 1 provides a yellow microcrystalline precipitate of [Ni(C(NHBu^t)Me)Cl(PMe$_3$)$_2$]Cl, **14a**, along with other unidentified nickel species. Compounds **14** and the related species **15**–**18** are best prepared by action of protonic acids on the neutral alkaneimidoyls, as shown in Scheme I.

The spectroscopic properties of these compounds are in agreement with their formulation as cationic aminocarbene complexes. Thus, their IR spectra exhibit two characteristic absorptions at 3570 and 3400 cm^{-1}, which can be attributed to the N–H bond of the aminocarbene ligand, which in addition gives rise to another characteristic absorption at ca. 1580–1560 cm^{-1}, due to ν(C=N). The proton attached to the nitrogen atom provides a broad NMR resonance centered at about 12.5 ppm, while the aminocarbene carbon produces a ^{13}C resonance at ca. 235 ppm, which appears as a triplet due to coupling to the two ^{31}P nuclei ($^2J_{CP} \simeq 30$ Hz). Similar shifts in the values of ν(C=N) and of δ(M—^{13}C=NR) upon protonation have been observed for other related systems.[5a,8b] On the other hand, the strong deshielding of the metal-bound carbon is clearly indicative of a significant contribution of the carbene resonance structure B.



The protonation reactions can be readily reversed: addition of base to solutions of the cationic aminocarbene species produces the original η^1-alkaneimidoyls. Thus the stirring of **14a** with powdered NaOH yields the methyl complex **1**. Workup proves however tedious due to side reactions. A more convenient deprotonating procedure makes use of NaCp, as depicted in eq 6.

$$\underset{\textbf{14a}}{[\mathrm{Ni(C(NHBu^t)Me)Cl(PMe_3)_2]Cl}} + \mathrm{NaCp} \rightarrow \underset{\textbf{1}}{\mathrm{Ni}[\eta^1\text{-}\mathrm{C(NBu^t)Me]Cl(PMe_3)_2}} + \mathrm{C_5H_6} + \mathrm{NaCl} \quad (6)$$

Experimental Section

Microanalyses were by Pascher, Microanalytical Laboratory, Bonn. The spectroscopic instruments were Perkin-Elmer Models 577 and 684 for IR spectra and Varian XL-200 for NMR. The ^{13}C resonance of the solvent was used as the internal standard, but chemical shifts are reported with respect to SiMe$_4$. ^{31}P NMR shifts are referenced to external 85% H$_3$PO$_4$. All preparations and other operations were carried out under oxygen-free nitrogen, following conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had boiling point of 40–60 °C. NaS$_2$CNMe$_2$ was dried by heating at 90 °C under vacuum for 2–3 days. PMe$_3$[26] and CNBu^{t}[27] were prepared according to literature methods, as were the compounds Ni(R)Cl(PMe$_3$)$_2$ (R = Me,[28] CH$_2$CMe$_2$Ph,[11a] CH$_2$SiMe$_3$,[11a] CH$_2$CMe$_3$[11b]), Ni(cod)$_2$,[29] and Ni(R)(NC$_4$H$_2$X$_2$)(PMe$_3$)$_2$.[17]

Preparation of Ni[η^1-C(NBu^t)Me]Cl(PMe$_3$)$_2$ (1). To a cold (−40 °C) solution of Ni(Me)Cl(PMe$_3$)$_2$ (0.67 g, 2.6 mmol) in Et$_2$O (40 mL) was added CNBu^t (0.3 mL, 2.6 mmol) via syringe, and the resulting mixture was stirred at room temperature for 3 h. After removal of the solvent in vacuo, extraction with Et$_2$O, and centrifugation, cooling at −30 °C provided compound 1 as orange needles in 80% yield.

Following a similar procedure, compound 2 was obtained as yellow crystals in 75% yield (from petroleum ether–Et$_2$O, −30 °C).

Reaction of Ni(CH$_2$SiMe$_3$)Cl(PMe$_3$)$_2$ with 1 Equiv of CNBu^t. A solution of Ni(CH$_2$SiMe$_3$)Cl(PMe$_3$)$_2$ (0.33 g, 1 mmol) in Et$_2$O (20 mL) at −40 °C was treated with 1 equiv of CNBu^t. After 3 h of stirring at room temperature, the volume was reduced in vacuo, and a mixture of petroleum ether–Et$_2$O (1:2, 20 mL) was added via syringe. After centrifugation, the solution was cooled at −30 °C to furnish yellow crystals of 5 (10–20% yield). From the mother liquor several crops of mixtures of 5 and 3 and eventually pure red crystalline 3 (30–40% yield) can be obtained after concentration and cooling at −30 °C. The combined yeild was 70%.

Compounds 4 and 6 were obtained in similar yields by using the above procedure.

Preparation of 3 by the Reaction of 5 with PMe$_3$. To a stirred solution of Ni[η^2-C(NBu^t)CH$_2$SiMe$_3$]Cl(PMe$_3$) (0.16 g, 0.5 mmol) in Et$_2$O (20 mL) was added a slight excess of PMe$_3$ (0.7 mL, 0.7 mmol). After 30 min of stirring at room temperature, the reaction mixture was evaporated in vacuo at 0 °C, and the resulting solid residue shown to be pure 3 by IR spectroscopy.

Formation of 5 from Complex 3. A solution of Ni[η^1-C(NBu^t)CH$_2$SiMe$_3$]Cl(PMe$_3$)$_2$ (0.46 g, 1.1 mmol) in 25 mL of Et$_2$O was heated at 40 °C in a glass ampule. After 2 h of stirring the

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solvent was evaporated, and additional Et_2O (25 mL) added to the solid residue. This cycle was repeated three times. An IR analysis of the material obtained showed that ca. 50% of **3** had been converted to **5**. The two products were separated by fractional crystallization as described above.

Preparation of Ni[η^2-C(NBu^t)CH$_3$](NC$_4$H$_2$Me$_2$)(PMe$_3$) (8). CNBu^t (0.23 mL, 2 mmol) was added to a cold (-40 °C), stirred, orange solution of Ni(Me)(NC$_4$H$_2$Me$_2$)(PMe$_3$)$_2$ (0.69 g, 2 mmol) in Et_2O (40 mL). The reaction mixture was allowed to reach room temperature and further stirred for 5 h, when the solution changed to red. After removal of the volatiles in vacuo, compound **8** was obtained as red crystals (45% yield) by extraction of the residue with a mixture of petroleum ether-Et_2O (2:1, 30 mL), filtration, concentration, and cooling at -30 °C.

The red complexes **7** and **10** were obtained in ca. 40% yield following a similar procedure. However, in the preparation of the yellow (trimethylsilyl)methyl derivative **9** traces of humidity should be very carefully avoided as water easily converts compound **9** into the analogous methyl derivative **8**. To purposefully achieve this transformation, to a solution of **9** in acetone was added one drop of water. After it was stirred for 30 min at room temperature, the solution changed from yellow to red. NMR spectroscopy shows the presence of compound **8** in the reaction mixture from which it can be isolated by crystallization from petroleum ether-Et_2O.

Synthesis of CpNi[η^1-C(NBu^t)CH$_3$]PMe$_3$ (11). Complex **1** (0.53 g, 1.5 mmol) was dissolved in Et_2O (30 mL), and the resulting solution cooled at -40 °C and reacted with 1 equiv of NaCp (2 mL of a 0.8 N solution in THF) added via syringe. The mixture was stirred for 3 h at room temperature, when the color changed to dark red. The volatiles were removed in vacuo, and the residue extracted with petroleum ether-Et_2O (1:1). Dark red crystals were obtained in 60% yield by centrifugation, partial removal of the solvent, and cooling at -30 °C.

Following a similar procedure, compound **12** was obtained as dark red crystals in 70% yield (from petroleum ether at -30 °C).

Preparation of Ni[η^1-C(NBu^t)Me](S$_2$CNMe$_2$)PMe$_3$ (13). An excess of dried, finely ground NaS$_2$CNMe$_2$ (0.21 g, 1.5 mmol) was added as a solid to a stirred solution of complex **1** (0.34 g, 1 mmol) in THF (30 mL). After stirring for 12 h at room temperature, the mixture was taken to dryness and the residue extracted with petroleum ether-Et_2O (1:2, 30 mL). Filtration, concentration of the resulting solution, and cooling at -30 °C furnished the desired product as red crystals in 75% yield.

Synthesis of [Ni(C(NHBu^t)Me)Cl(PMe$_3$)$_2$]BF$_4$ (14b). To a stirred, cold (-40 °C) solution of complex **1** (0.34 g, 1 mmol) in Et_2O (30 mL) was added 1.5 equiv of HBF$_4$ (0.3 mL of a 35% solution in water). The formation of a precipitate was noted, and the resulting suspension was stirred at room temperature for 30 min. The yellow product was filtered and dried in vacuo to afford **14b** in almost quantitative yield. An analytical sample was obtained, in the form of yellow-orange crystals upon crystallization of the crude product from toluene-CH$_2$Cl$_2$ at -40 °C.

By adding aqueous solutions of HCl and HNO$_3$ to **1**, the corresponding chloride (**14a**) and nitrate (**14c**) salts were similarly obtained. The tetraphenyl borate salt (**14d**) was prepared from **14a** and NaBPh$_4$ in acetone. After evaporation of the solvent, the residue was crystallized from toluene-CH$_2$Cl$_2$.

By use of an essentially similar procedure, the following compounds were obtained by using complexes **4**, **11**, **12**, and **13** as starting materials: [Ni(C(NHBu^t)CH$_2$CMe$_3$)Cl(PMe$_3$)$_2$]BF$_4$ (**15**), yellow crystals; [CpNi(C(NHBu^t)Me) (PMe$_3$)]BF$_4$ (**16**), green crystals; [CpNi(C(NHBu^t)CH$_2$CMe$_2$Ph)(PMe$_3$)]BF$_4$ (**17**), green crystals; [Ni(C(NHBu^t)Me)(S$_2$CNMe$_2$)(PMe$_3$)]BF$_4$ (**18**), yellow-brown crystals, respectively.

Deprotonation of Complex 14b. A suspension of **14b** (0.34 g, 0.9 mmol) in a mixture of Et_2O-THF (1:1, 30 mL) was cooled at -60 °C, and NaCp was added (0.9 mL of a 1 M solution in THF) via syringe. After 3 h of stirring at room temperature, the volatiles were removed in vacuo, and the residue was extracted with a mixture of petroleum ether-Et_2O. Centrifugation, partial removal of the solvent, and cooling at -30 °C furnished compound **1** in 60% yield.

Deprotonation with powdered NaOH could also be effected, but workup of the reaction is difficult due to side reactions that afford hydroxo complexes of nickel.

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Electronic Structure of the Nonclassical Trimetallic Alkyne Cluster Complex Os$_3$(CO)$_9$(μ-H)$_2$(μ_3-HC$_2$NEt$_2$)

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The electronic structure of the new 48-electron basketlike cluster compound Os$_3$(CO)$_9$(μ-H)$_2$(μ_3-HC$_2$NEt$_2$) is compared to that of 46-electron closo and 48-electron nido M$_3$C$_2$ complexes. The unusual coordination of the alkyne ligand is attributed to the diethylamino group linked to one of the carbon atoms of the alkyne moiety.

To date, trimetallic alkyne cluster complexes have been encountered in two distinct geometries separated by their electron counts. Those characterized by 46 cluster valence electrons (CVE's), or 6 skeletal electron pairs (SEP's),[1] adopt a closo trigonal-bipyramidal structure (**1**) with the alkyne moiety lying perpendicular to one metal-metal bond. The others, possessing 48 CVE's or 7 SEP's, describe a nido square-pyramidal geometry (**2**), the acetylenic ligand positioned parallel to a metal-metal vector. In each case the neutral acetylene is counted as a 4-electron ligand. The recent synthesis and structure determination by two

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