Applying the Macrocyclic Effect to Smaller Ring Structures. *N,N′*-Dimethyl-3,7-diazabicyclo[3.3.1]nonane Nickel(0) Complexes[†]

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Abstract: The two N donor atoms in the tertiary diamine *N,N′*-dimethyl-3,7-diazabicyclo[3.3.1]nonane (dabn, $C_9H_{18}N_2$) are ideally positioned in the bicyclic structure for chelation to a metal center. This feature was utilized to synthesize unusual diamine nickel(0)−ethene and −ethyne complexes, which represent limiting cases of the Pearson hard-soft acid-base concept. Thus, the reaction of $Ni(C_2H_4)_3$ with dabn affords yellow *TP*-3 $(C_9H_{18}N_2)Ni(C_2H_4)$ (**1**) (dec. 0 °C) in which the ethene ligand displays extreme high-field NMR shifts at $\delta(H)$ 0.27 and $\delta(C)$ 20.4 and an exceptionally small coupling constant $^1J(CH) = 142$ Hz. Reaction of **1** with butadiene yields the red mononuclear *T*-4 complex $(C_9H_{18}N_2)Ni(\eta^2\text{-}C_4H_6)_2$ (**2a**) in solution, from which the dinuclear derivative $\{(C_9H_{18}N_2)Ni(\eta^2\text{-}C_4H_6)\}_2(\mu\text{-}\eta^2,\eta^2\text{-}C_4H_6)$ (**2**) (dec. 20 °C) is isolated. Complexes **2** and **2a** are more soluble than **1** and thus better suited for further reactions. When ethyne is added to a solution of **2** or **2a** at −78 °C, the yellow *TP*-3 complex $(C_9H_{18}N_2)Ni(C_2H_2)$ (**3**) (dec. −30 °C) is obtained. The ethyne ligand of **3** exhibits the lowest IR C≡C stretching frequency (1560 cm^{-1}) and by far the smallest NMR coupling constant $^1J(CH) = 178$ Hz yet reported for a mononuclear nickel(0)−ethyne complex. In addition, $Ni(CO)_4$ reacts with dabn to yield orange *T*-4 $(C_9H_{18}N_2)Ni(CO)_2$ (**4**). The results demonstrate that tertiary diamines, which are hard Lewis bases and which a priori are expected to coordinate poorly to the soft Lewis acid Ni(0), may be supported in such a coordination by the stabilizing principle of preorganization and consequently act as very powerful donor ligands.

Introduction

According to the Pearson hard-soft acid-base (HSAB) concept of acids and bases, amines are hard bases and Ni(0) is a soft acid,[1] and thus, the coordination of amines to Ni(0) is predicted to be unfavorable. This is expected to be particularly the case when Ni(0) is coligated by a nonactivated alkene such as ethene. We were therefore surprised to find that one ethene ligand in $Ni(C_2H_4)_3$[2] can be readily displaced by an amine [e.g., NH_3, Et_2NH, quinuclidine ($C_7H_{13}N$)] to yield trigonal-planar (*TP*-3) complexes of the type (amine)$Ni(C_2H_4)_2$. An X-ray analysis of $(C_7H_{13}N)Ni(C_2H_4)_2$ (dec. 0 °C) reveals a long Ni−N bond (2.07 Å).[3] This type of complex must be distinguished from the more stable Strohmeier type complexes, such as $(C_7H_{13}N)\text{-}Cr(CO)_5$,[4] in which the carbonyl ligands induce a fairly large electron withdrawal from the metal(0) center, rendering the latter somewhat harder and consequently more suited for complexing a hard amine ligand. This tendency is also seen in the reaction of $Ni(CO)_4$ with liquid NH_3 at 20 °C (sealed tube), which affords a mixture of the presumed complexes $(NH_3)Ni(CO)_3$ and $(NH_3)_2Ni(CO)_2$ in solution, which upon isolation decompose at −60 °C.[5,6] In accord with the increased stability of the CO

complexes, $(C_7H_{13}N)Ni(C_2H_4)_2$ reacts with CO to yield pure $(C_7H_{13}N)Ni(CO)_3$ (dec. > 0 °C).[3]

Following from these studies on (amine)$Ni(C_2H_4)_2$ type complexes, we were interested in the question as to whether complexes of the inverse stoichiometry (amine)$_2Ni(C_2H_4)$ would also be stable and whether an ethyne derivative (amine)$_2Ni(C_2H_2)$ could be prepared. In these complexes, the charge transferred to Ni(0) by *two nitrogen donor atoms* has to be accommodated by back-bonding to a *single π-ligand*. Since these complexes are expected to be inherently labile, we embarked on a project to study ways of stabilizing them, and the results of this work[7] are reported here.

Results

According to current knowledge, it does not appear likely that any (amine)$_2Ni(C_2H_4)$ complex with two monodentate amine ligands is stable enough to be synthesized by classical wet chemistry. An *ab initio* MO-SCF calculation[8] on the simplest homolog $(NH_3)_2Ni(C_2H_4)$ predicts the molecule to be thermodynamically stable. This complex may possibly be formed as a transient species, e.g., by the reaction of a $Ni(0)(NH_3)_2$ matrix[9] with ethene. However, all attempts to

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[†] Part VII of our series *Amine-Nickel(0) Complexes*. For part VI see ref 15.

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(6) A 1:1 mixture of $Ni(CO)_4$ and tmeda is yellow at 20 °C and orange at 30 °C but no CO evolves. After some pentane has been added, no product crystallizes at −78 °C. This and other observations suggest that [(tmeda)-$Ni(CO)_2$] cannot be isolated. Moreover, it is expected that [(tmeda)-$Ni(CO)_2$] if formed will readily disproportionate into $[Ni(tmeda)_2]^{2+}$-$[Ni_6(CO)_{12}]^{2-}$, cf., the characterization of $(NH_3)Ni(CO)_3$ and $(NH_3)_2Ni(CO)_2$ in ref 5.

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synthesize and isolate the compound have so far been unsuccessful. In the hope of introducing some stability by the chelate effect, we scrutinized various structural types of *bidentate amines* for their suitability as ligands for Ni(0).

(a) Tetramethylethylenediamine (tmeda). When tmeda is added to a pentane solution of $Ni(C_2H_4)_3$ at -78 °C, the yellow color intensifies, but no diamine complex is observed. We assume that the dinuclear complex $(C_2H_4)_2Ni(\mu$-$Me_2NC_2H_4$-$NMe_2)Ni(C_2H_4)_2$ is in equilibrium with tmeda and $Ni(C_2H_4)_3$. In $(C_2H_4)_2Ni(\mu$-$Me_2NC_2H_4NMe_2)Ni(C_2H_4)_2$, the bridging tmeda ligand is part of two $(amine)Ni(C_2H_4)_2$ type moieties. The species $[(tmeda)Ni(C_2H_4)]$, containing a chelating tmeda ligand, is not observed in the solution.[3] The same is true for N,N,N',N'-tetramethyl-1,3-propanediamine. Thus, it would appear that for *acyclic diamines* with N atoms in the 1,4- or 1,5-positions, no Ni(0)−*ethene* complex of the type $(amine)_2Ni(C_2H_4)$ with a chelating diamine ligand is isolable. A likely explanation is that the π-acceptor strength of ethene is not large enough to make Ni(0) sufficiently electrophilic to bind two tertiary amine N atoms when their coordination is merely supported by an open-chain-ligand chelate effect.[10,11]

The situation is somewhat different when the coligands have stronger π-accepting properties than ethene. For example, the reaction of the tmeda/$Ni(C_2H_4)_3$ system with butadiene results in the isolation of the dinuclear complex $\{(tmeda)Ni(\eta^2$-$C_4H_6)\}_2(\mu$-η^2,η^2-$C_4H_6)$ (dec. -40 °C), and $(tmeda)Ni(\eta^2$-$C_4H_6)_2$ is observed in solution.[12] When methyl acrylate is employed, the complex $(tmeda)Ni(H_2C=CHCOOMe)_2$ (dec. 110 °C) can be isolated.[13] Interestingly, tmeda/$Ni(C_2H_4)_3$ reacts with formaldehyde to yield $(tmeda)Ni(C_2H_4)(CH_2O)$ (dec. -15 °C), in which the joint coordination of chelating tmeda and ethene to Ni(0) is facilitated by the additional $H_2C=O$ ligand.[14] In these tmeda complexes, which contain π-ligands of moderate acceptor strength (butadiene, $H_2C=CHCOOMe$, $H_2C=O$), the 18 e Ni(0) center is tetrahedrally (*T*-4) coordinated. The 16 e *TP*-3 Ni(0) complexes with chelating tmeda are only known for strong π-acceptor ligands such as stilbene, maleic acid anhydride, diphenylacetylene, tetrafluoroethene, or benzophenone, of which $(tmeda)Ni(C_2F_4)$[15] and $(tmeda)Ni(O=CPh_2)$[16] are structurally characterized examples. A corresponding *ethyne* complex $[(tmeda)Ni(C_2H_2)]$ is not accessible, for as soon as an appropriate synthesis is attempted, ethyne polymerizes instantaneously at -100 °C, thereby reacting as if "naked nickel" were present.[17] For ethyne, the electron withdrawal from Ni(0) by the ethyne ligand is possibly sufficient to stabilize the tmeda coordination

at Ni(0), but the tmeda ligand influence is too weak to deactivate the π-coordinated ethyne and prevent its polymerization.

(b) 1,4-Diazacyclohexane, 1,5-Diazacyclooctane, and Their *N,N'*-Dimethyl-Substituted Derivatives. We then looked at the *monocyclic diamines*, 1,4-diazacyclohexane (piperazine), 1,5-diazacyclooctane (daco) and their N,N'-dimethyl-substituted derivatives, where the conformational freedom of the ligand is restricted. For (N,N'-dimethyl) piperazine the boat conformation necessary for a chelating coordination (**A**) is energetically unfavorable as compared with the chair conformation due to the torsional strain of the neighboring methylene groups.[18a]
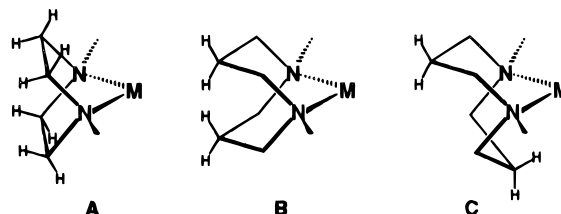
Hence, the required energy to attain the boat conformation has to be gained from the formation of strong metal−nitrogen bonds, which is only the case when the diamine is coordinated to *metal ions*. Thus, $\{MeN(C_2H_4)_2NMe\}PdCl_2$[18b] has been isolated, but in general (N,N'-dimethyl) piperazine complexes are rare.[18c,d]

Several complexes are known in which daco chelates to *metal ions*.[19] Coordination results in the formation of two metalla-cyclic six-membered rings, as well as the original eight-membered daco ring. If both six-membered rings attained the chair conformation (**B**), then the torsional strain in each ring is the least, but the 3,7-methylene groups interfere with each other in the eight-membered ligand. Consequently, the chair/chair conformation cannot be realized by the daco ligand. If a chair/boat combination (**C**) is present, then the transannular interaction of the methylene groups in the eight-membered ligand ring is avoided, but the boat-shaped six-membered ring has an increased energy due to the torsional strain caused by four C−H bonds being eclipsed to N−C bonds. (For the same reason a hypothetical boat/boat conformation can be dismissed here.) Nevertheless, the chair/boat and an energetically similar chair/semiboat conformation have been observed in certain complexes.[19] It follows from these arguments that the daco molecule can in fact only coordinate to a metal center in a chair/boat or chair/twisted-boat conformation. Both have a higher energy than the uncoordinated flexible diamine.

We have, however, not been able to synthesize a corresponding $(amine)_2Ni(C_2H_4)$ type complex with piperazine, daco, or their N,N'-dimethyl-substituted derivatives. If we assume that the expected $R_3N-Ni(0)$ coordinative bonds are inherently weak, then the energy gained by forming these bonds is clearly too low to compensate for the energy required by the diamine ligands to attain the required conformation for chelation. This also explains why the monocyclic diamines piperazine and daco, although coordinating to certain metal ions, do not coordinate to *neutral Ni(0)* in combination with ethene as coligand.[20]

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(11) In our experience, the species [(tmeda)Ni(0)] [145086-32-4] and [(tmeda)Ni(cod)] [121719-01-5], which have often been proposed as intermediates, but without experimental evidence,[11a,18d] are not formed to any significant extent in the system tmeda/Ni(0)/cod. This is indicated by the fact that when $Ni(cod)_2$ (500 mg) is dissolved in undiluted tmeda (25 mL) at 40 °C, it recrystallizes unchanged at -30 °C (430 mg; 86%). (a) Wenschuh, E.; Zimmering, R. *Z. Anorg. Allg. Chem.* **1989**, *570*, 93. Walther, D.; Bräunlich, G.; Kempe, R.; Sieler, J. *J. Organomet. Chem.* **1992**, *436*, 109. Fischer, R.; Walther, D.; Kempe, R.; Sieler, J.; Schönecker, B. *J. Organomet. Chem.* **1993**, *447*, 131. Kempe, R.; Sieler, J.; Walther, D.; Reinhold, J.; Rommel, K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1105.

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Table 1. ^{1}H and ^{13}C NMR Data of Uncoordinated dabn and the dabn Ligand of the Nickel(0) Complexes **1**−**4**[a]

	δ(H)					δ(C)			
	NCH$_{eq}$H	NCHH$_{ax}$	NCH$_3$	C$_{tert}$H	CH$_2$	NCH$_2$	NCH$_3$	C$_{tert}$H	CH$_2$
dabn	2.61	2.23	2.09	1.84	1.43	60.6	46.5	30.6	30.0
	^2J(HH) −11.0	^2J(HH) −11.0							
	^3J(HH) 2.8	^3J(HH) 4.6			^3J(HH) 3.3				
1	3.59	2.38	2.48	1.92	1.50	61.7	55.7	30.6	32.4
	^2J(HH) −11.4	^2J(HH) −11.4							
	^3J(HH) ≤ 1	^3J(HH) 2.6			^3J(HH) 3.3				
2a	3.83/3.04	2.43/2.11	2.16	1.98	1.56	63.0/62.2	50.8	30.8	34.3
3	3.55	2.42	2.60	1.99	1.53	62.5	56.3	30.6	32.3
	^2J(HH) −11.3	^2J(HH) −11.3							
4	3.37	2.56	2.72	2.05	1.61	65.6	54.5	31.8	33.2
	^2J(HH) −10.8	^2J(HH) −10.8							

[a] Coupling constants are in hertz. For instrument and temperature specifications, see the Experimental Section.

It follows that a diamine ligand suitable for coordination to the [Ni(0)(C$_2$H$_4$)] fragment can perhaps be derived from the 1,5-diazacyclooctane skeleton in its chair/chair conformation (**B**) by substituting the methylene protons, which exert the repulsive transannular interaction in the eight-membered ring, with a bridging methylene group. We therefore turned our attention to derivatives of 3,7-diazabicyclo[3.3.1]nonane (bis-pidine), which contains a rigid molecular scaffold and provides an apparently optimal arrangement of the N atoms for chelating a metal center.

(c) *N,N′*-Dimethyl-3,7-diazabicyclo[3.3.1]nonane (dabn, C$_9$H$_{18}$N$_2$). The bispidine skeleton[21−23] was synthesized by a double Mannich reaction of *N*-methyl-4-piperidone, formaldehyde, and methylamine to afford *N,N′*-dimethyl-3,7-diazabicyclo[3.3.1]nonan-9-one.[24,25] The bispidinone itself, which forms two conformers,[26] does not coordinate to the [Ni(0)(C$_2$H$_4$)] fragment. Wolff−Kishner reduction (hydrazine/triethyleneglycol) yields a mixture of dabn[24] and several byproducts, from which dabn was separated by rectification.

The conformation of dabn has been determined on the basis of its ^{1}H[24,27a] and ^{13}C[27b] NMR spectra (the latter in comparison with the ^{13}C NMR data of the bispidine derivatives (−)-sparteine and α-isosparteine), its dipole moment,[24] MO calculations,[27b,d] and EI-MS[27c] and photoelectron (PE)[27b] spectra. In addition, we have measured its high-resolution ^{1}H NMR spectrum and the IR and Raman (RA) spectra. In the ^{1}H NMR spectrum (Table 1), the signals of the NCH protons follow the rule δ(NCH$_2$) > δ(NCH$_3$) with inequivalent geminal protons NCH$_{eq}$H$_{ax}$. Assuming a chair conformation of both six-membered rings (see below), the protons NCHH_{ax} are shielded by 0.4 ppm more than the protons NCH$_{eq}$H, due to both a general

feature of six-membered rings and the σ-electron delocalization of the N atom lone pairs into the antiperiplanar C−H bonds.[28] It is worth noting that, in addition to the C−H stretching bands in the usual region of the dabn IR spectrum (2960, 2930, 2880, 2839 cm^{-1}), intense Bohlmann bands are observed at lower frequencies (2773, 2735, 2689 cm^{-1}). These Bohlmann bands can be likewise attributed to the NCHH_{ax} protons antiperiplanar to the N atom lone pairs.[29] A similar feature is found in the Raman spectrum. The observations are in agreement with the assumption that the N atom lone pairs formally take up axial positions, pointing to a common hypothetical coordination center and leaving the N−Me substituents in equatorial positions. As will be shown below, for (dabn)Ni complexes, the Bohlmann bands are substantially reduced while a strong band near 2800 cm^{-1} occurs. Thus, coordinative constraint of the nitrogen lone pairs weakens the delocalization into the antiperiplanar C−H bonds.

The various results are best summarized by the statement that liquid or dissolved dabn is present in *a flattened chair/chair conformation with the N−Me substituents in the equatorial positions* (**D**).[24,27a,30] It becomes evident that in dabn, due to

D
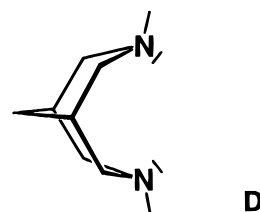
its particular bicyclic structure, the amine functions are almost ideally positioned for chelation and that this substrate is by far the best choice for attempting an otherwise unfavorable coordination of a diamine to the [Ni(0)(C$_2$H$_4$)] fragment.

(d) *N,N′*-Dimethyl-3,7-diazabicyclo[3.3.1]nonane−Nickel(0) Complexes. Following the arguments developed above, Ni(C$_2$H$_4$)$_3$ was reacted with dabn to yield the isolated (dabn)-Ni(0)−ethene complex **1**. From **1**, the (dabn)Ni(0)−butadiene (**2, 2a**) and (dabn)Ni(0)−ethyne (**3**) complexes are accessible.

(20) We did not study the combination of (*N,N′*-dimethyl-substituted) daco and activated alkenes with nickel(0). We expect the situation to be similar as that for the combination of tmeda with such alkenes, see above.

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(30) *Ab initio* calculations on the parent bispidine (NH instead of NMe) suggest the chair/chair conformation to be present in 80% in the gas phase. For dabn, a flattened chair/chair conformation is assumed to predominate on the basis of the PE spectrum and various MO calculations; a concentration of 99.8% is predicted by a MINDO/3 calculation. It may be concluded that the predominance of the chair/chair conformer of the bispidine skeleton is supported by the N−CH$_3$ substituents.[27b]

Table 2. Ethene and Ethyne Ligand NMR and IR Data of the (dabn)Ni(0) Complexes **1** and **3** and of Reference Compounds

	δ(H)	δ(C)	^1J(CH) [Hz]	ν(C=C) [cm^{-1}]	ν(C≡C) [cm^{-1}]
C_2H_4	5.30	123.5	156	1623[a]	
(ArN=CHCH=NAr)Ni(C$_2$H$_4$)$_2$[36][b]	2.42	64.9	154		
(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Ni(C$_2$H$_4$)[42]	1.74	31.6	151	1530	
(bpy)Ni(C$_2$H$_4$)[37]	1.59	26.7	146		
(dabn)Ni(C$_2$H$_4$) (**1**)	0.27	20.4	142	1510	
(tmeda)$_2$(LiC$_2$H$_5$)$_2$Ni(C$_2$H$_4$)[55a]	−0.83	2.3	129		
C_2H_2	2.40	71.9	249		1974[a]
(Ph$_3$P)$_2$Ni(C$_2$H$_2$)[43a]	6.41	122.1	212		1630
(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Ni(C$_2$H$_2$)[42]	7.29	123.8	202		1598
(^{t}BuN=CHCH=N^{t}Bu)Ni(C$_2$H$_2$)[59]	4.46	114.0	197		
(dabn)Ni(C$_2$H$_2$) (**3**)	4.65	118.7	178		1560

[a] Gas phase; Raman. [b] Ar = C$_6$H$_3$-2,6-^{i}Pr$_2$.

The (dabn)Ni(0)-CO complex **4** was prepared from dabn and Ni(CO)$_4$.

(C$_9$H$_{18}$N$_2$)Ni(C$_2$H$_4$) (1). The reaction of Ni(C$_2$H$_4$)$_3$ with dabn in diethyl ether at −10/−30 °C results in displacement of two ethene ligands from Ni(0) and precipitation of yellow microcrystalline **1** in 83% yield (eq 1). Below −30 °C the reaction
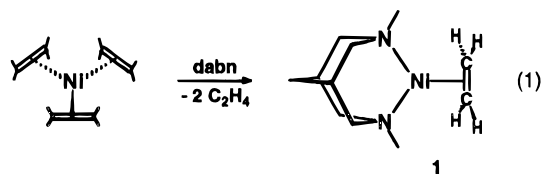
is very slow. Complex **1** is insoluble in diethyl ether or pentane and dissolves sparingly in THF or toluene at −30 °C. In solution, the product slowly decomposes above this temperature, whereas the solid is stable to about 0 °C. It is therefore important for a successful synthesis that the product rapidly precipitates from the solution.

Chemical Properties. The reactivity of **1** toward CO, 1,5-cyclooctadiene (cod), ethene, and ethyne has been studied. A yellow suspension of complex **1** in diethyl ether or THF reacts at −30 °C with 4 equiv of CO by displacing all ligands from Ni(0) to yield—via the intermediate (C$_9$H$_{18}$N$_2$)Ni(CO)$_2$ (**4**; see later)—a colorless solution of Ni(CO)$_4$. Similarly, when cod is added to a suspension of **1** at −30 °C, the complex slowly converts into the yellow precipitate of Ni(cod)$_2$ (identified by its IR spectrum).[31] These facile reactions that afford typical Ni(0) complexes indicate that, in complex **1**, (a) Ni is indeed in the oxidation state 0 and (b) the coordination of the ligands to Ni(0) is relatively weak. However, the exchange of the ethene ligand with uncoordinated ethene is rather slow. This has been shown for a THF-d_8 solution of **1** saturated with ethene, which exhibits in the ^{1}H NMR spectrum (80 MHz) at −80 °C sharp and at −20 °C somewhat broadened but separate signals for uncoordinated (δ 5.30) and coordinated ethene (δ 0.27; see below). When a suspension of **1** in diethyl ether is treated in an autoclave with 55 bar of ethene at 20 °C for several hours, no reaction is observed, i.e., the formation of a nickelacyclopentane [(C$_9$H$_{18}$N$_2$)Ni(C$_4$H$_8$)], a catalytic ethene dimerization (butene isomers, cyclobutane), or oligo/polymerization does not occur. Instead, after discharging the autoclave, complex **1** is partially recovered. It appears that the otherwise thermally labile complex **1** is stabilized by additional ethene.[32] Furthermore, complex **1** suspended in THF or diethyl ether reacts only very slowly with ethyne at −78 °C. Most of the ethyne polymerizes in time, although in solution (THF-d_8) the formation of the Ni(0)−ethyne complex **3** (see below) has been detected by ^{1}H NMR. The incomplete formation of complex **3** from **1** is attributed to the low solubility and hence low reactivity of **1** at −78 °C. These results correspond to our general observation

that a fast low-temperature reaction in homogeneous solution is required for a successful synthesis of labile Ni(0)−ethyne complexes.[33]

Spectroscopical Properties. In the EI mass spectrum of **1** the molecular ion and the fragment [(dabn)Ni]$^+$ are detected, but the overall spectrum essentially corresponds to that of uncoordinated dabn. The IR spectrum (KBr) is dominated by vibrations of dabn coordinated to Ni(0). Additional bands which we assign to the ethene ligand[34] [ν(C=C) + δ_s(CH$_2$) = 1510 cm^{-1}] are comparatively strongly shifted by complexation. In the ^{1}H NMR spectrum of **1**, the dabn ligand signals (Table 1) are all shifted to low field as compared with those of uncoordinated dabn, and this shift is strongest for the NCH_{eq}H ($\Delta\delta$ = −1.0 ppm) and NCH$_3$ ($\Delta\delta$ = −0.4 ppm) protons. Such changes are less pronounced in the ^{13}C NMR spectrum (Table 1), for which the low-field shift is strongest for NCH$_3$ ($\Delta\delta$ = −9 ppm). In contrast to dabn, the ethene ligand proton and carbon resonances of δ(H) 0.27 and δ(C) 20.4 lie at extremely high field, and the coupling constant ^1J(CH) = 142 Hz is extraordinary low [typical range for Ni(0)−ethene complexes is 155 − 151 Hz; for examples and exceptions to the rule, see Table 2].

Unfortunately, it has not been possible to obtain crystals suitable for an X-ray analysis, so the exact coordination is not known. On the basis of spectroscopic data, **1** probably contains a *TP*-3 Ni(0) center coordinated by the dabn N atoms and the ethene ligand with its C atoms in the coordination plane (planar conformation). Although no information is available about possible rotation of the ethene ligand about the bond axis to the nickel atom, we expect the bonding to be static as is found for other L$_2$Ni−alkene complexes.[35]

Complex **1** is the only (diamine)Ni(0)−alkene complex containing a nonactivated alkene ligand (ethene) that has been isolated so far. It is important to distinguish this complex from (N-donor)Ni(0)−ethene complexes such as *T*-4 (2,6-^{i}Pr$_2$C$_6$H$_3$N=CHCH=NC$_6$H$_3$-2,6-^{i}Pr$_2$)Ni(C$_2$H$_4$)$_2$[36] and *TP*-3 (bpy)Ni(C$_2$H$_4$) (bpy = 2,2′-bipyridine).[37a] In these compounds the hybridization of the N atoms in the ligands is sp^2, bringing the ligands into the category of soft base. In contrast, dabn with its sp^3-hybridized N atoms must be considered a hard base. The ethene ligand NMR data of the (N-donor)Ni(0)−ethene

(31) Bogdanovic, B.; Kröner, M.; Wilke, G. *Liebigs Ann. Chem.* **1966**, *699*, 1.

(32) It cannot be ruled out that the dabn ligand is reversibly displaced from Ni(0) when complex **1** is pressurized with ethene to form Ni(C$_2$H$_4$)$_3$ (which is itself stabilized by ethene).

(33) Pörschke, K.-R. *J. Am. Chem. Soc.* **1989**, *111*, 5691.

(34) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, **1978**; p 383.

(35) Pörschke, K.-R.; Pluta, C.; Proft, B.; Lutz, F. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1993**, *48*, 608.

(36) Bonrath, W.; Pörschke, K.-R.; Michaelis, S. *Angew. Chem.* **1990**, *102*, 295; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 298.

complexes (Table 2) indicate an increase in back-bonding from Ni(0) to the ethene ligand in the sequence 1,4-diazabutadiene < bpy[37b,c] < dabn.

Hence, it appears that dabn is the by far the strongest N-donor ligand to nickel(0), which is consistent with the fact that its sp^3-hybridized N atoms are simple σ-donors and lack a mitigating π-acceptor ability.

{$(C_9H_{18}N_2)Ni(\eta^2\text{-}C_4H_6)$}$_2(\mu\text{-}\eta^2,\eta^2\text{-}C_4H_6)$ (2) and ($C_9H_{18}N_2$)-Ni($\eta^2\text{-}C_4H_6$)$_2$ (2a). A yellow suspension of **1** in diethyl ether reacts at −30 °C with butadiene by displacement of the ethene ligand to afford a red solution of the (nonisolated) mononuclear complex **2a** (for NMR characterization, see below). Small dark red cubes of complex **2** slowly separate from this solution at −78 °C (eqs 2 and 3). Crystalline **2** decomposes at 20 °C with
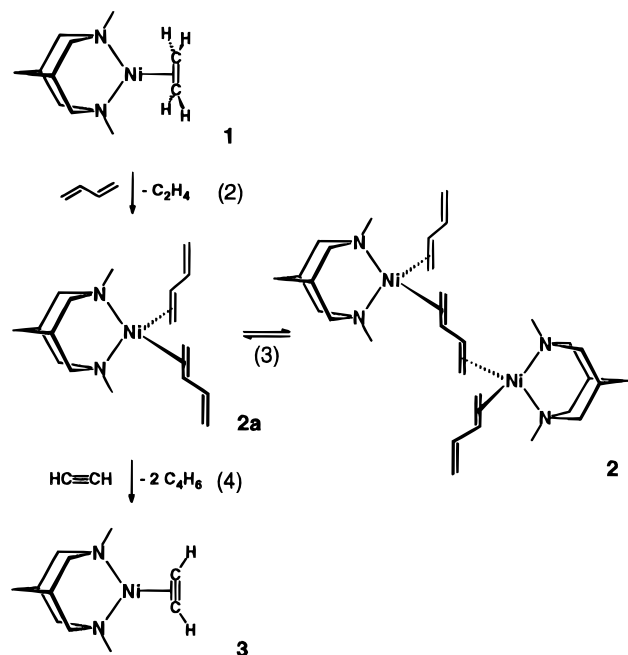
elimination of butadiene. At −78 °C, the complex dissolves poorly in diethyl ether or pentane but quite well in THF and toluene, thereby reforming **2a**. The red solutions are stable to about 0 °C and produce a black precipitate (metallic nickel) above this temperature.

In the EI mass spectrum of **2**, the largest observable ion is [(dabn)Ni(C$_4$H$_6$)]$^+$, which fragments by cleaving the butadiene ligand to afford [(dabn)Ni]$^+$. In the IR spectrum (KBr), various bands in addition to the dabn modes due to (inequivalent) butadiene ligands are observed. On the basis of the composition of the complex (elemental analysis), its properties, and the analogy to similar systems, the dinuclear structure of complex **2** is beyond doubt. In **2** both Ni atoms are *T*-4 coordinated by the bidentate dabn ligand with a singly bound butadiene ligand and a butadiene ligand bridging the Ni centers. Compound **2** is analogous to the bpy complex {(bpy)Ni(η^2-C$_4$H$_6$)}$_2$(μ-η^2,η^2-C$_4$H$_6$), for which a dinuclear structure has been confirmed by an X-ray crystal structure analysis,[38] and to the tmeda derivative

(37) (a) Mayer, W.; Pörschke, K.-R.; Krüger, C. Unpublished results (1978). (b) It follows from the ^{1}H and ^{13}C NMR data of (bpy)Ni(C$_2$H$_4$) (Table 2), from the similar constitutions and NMR data of the (dabn, tmeda, bpy)Ni(0)−butadiene complexes, and from the very small coupling constant $^1J(\text{CH}) < 190$ Hz for the complexes (bpy)Ni(HC≡CR) [(bpy)Ni(HC≡CH) is not stable] that bpy is a stronger donor ligand for Ni(0) than are phosphanes. Pörschke, K.-R.; Bonrath, W.; Michaelis, S. Unpublished results. (c) Anisotropy effects of the bpy ligand on the chemical shifts of the ethene ligand of (bpy)Ni(C$_2$H$_4$) are presumably small.
(38) Mayer, W.; Wilke, G.; Benn, R.; Goddard, R.; Krüger, C. *Monatsh. Chem.* **1985**, *116*, 879.

{(tmeda)Ni(η^2-C$_4$H$_6$)}$_2$(μ-η^2,η^2-C$_4$H$_6$) already mentioned (the latter decomposes at −40 °C and is thus markedly less stable than **2**). As detailed NMR studies have shown, these dinuclear bpy and tmeda complexes dissociate in solution (THF, toluene) into the mononuclear *T*-4 complexes (bpy)Ni(η^2-C$_4$H$_6$)$_2$ and (tmeda)Ni(η^2-C$_4$H$_6$)$_2$, respectively, to which **2a** is in turn related.[39] It appears that, in the N-donor/Ni(0)/butadiene system, the mononuclear butadiene complexes represent the basic coordination mode of Ni(0) in solution, whereas the dinuclear complexes separate from the solutions due to their lower solubility.

NMR Characterization of 2a. The ^{1}H and ^{13}C NMR spectra of a THF-d_8 solution of **2** (−80 °C) display relative signal intensities dabn:butadiene of 1:2. The butadiene ligands show six proton and four carbon signals of equal intensities for one type of coordinated and one type of uncoordinated C=C bond. The dabn ligand (Table 1) exhibits seven proton and five carbon signals, indicating that the symmetry of the complex is reduced to C_2 (as compared with the more symmetric **1**, **3**, and **4**). The coupling constant of the butadiene =CH− protons of $^3J(\text{HH})$ = 10.5 Hz indicates a *trans* conformation with respect to the central single bond.[40] The spectra are consistent with a *T*-4 Ni(0) center coordinated by the dabn N atoms and two equivalent, singly bound, *single-trans* butadiene ligands. The substituted C atoms of the coordinated butadiene C=C bonds are chiral due to the complexation[41] and necessarily of the same configuration (*R,R* or *S,S*) consistent with the C_2 symmetry of the complex. Thus, the spectra are assigned to the racemate **2a** (only one enantiomer is depicted in eqs 2−4).

No exchange of the coordinated and uncoordinated butadiene C=C bonds of **2a** takes place at −80 °C on the NMR time scale. The NMR spectra give no information regarding a possible rotation of the coordinated C=C bonds about the coordination axis to the Ni atom. When the temperature is raised, all signals broaden and a dynamic process, which has not been investigated further, occurs. In the 80 MHz ^{1}H NMR spectrum, the signals are broad up to 0 °C, at which temperature **2a** decomposes.

The low-temperature ^{1}H and ^{13}C NMR resonances of the dabn NCH$_2$ and NMe groups and the butadiene ligands of **2a** almost coincide with those of (tmeda)Ni(η^2-C$_4$H$_6$)$_2$.[12] Bearing in mind that the composition and chemical properties of the respective dabn (**2**, **2a**) and tmeda complexes are also alike, it can be concluded that tmeda and dabn, if coordinated to Ni(0), will exhibit similar electronic effects.

($C_9H_{18}N_2$)Ni(C_2H_2) (3). When a red slurry of the (dabn)-Ni(0)−butadiene complex **2** in diethyl ether is exposed to excess ethyne at −78 °C, **2** dissolves and a yellow precipitate of **3** is formed in moderate yield (42%) (eq 4). Solid **3** decomposes above −30 °C. The complex is almost insoluble in pentane or diethyl ether and dissolves poorly in THF or toluene at −78 °C. The solutions are only stable below −60 °C. Complex **3** is thus far the only reported Ni(0)−ethyne complex that is exclusively stabilized by an amine ligand.

Spectroscopic Properties and Structure. In the IR spectrum of **3**, the sharp C≡C stretching band of the ethyne ligand appears

(39) The equilibrium between the dinuclear complexes, containing 1.5 butadiene ligands per Ni atom, and the mononuclear species is complicated because the mononuclear complexes contain 2 butadiene ligands per Ni atom. For the systems, tmeda/Ni(0)/C$_4$H$_6$[12] and dabn/Ni(0)/C$_4$H$_6$, neither [(tmeda)Ni(C$_4$H$_6$)] nor [(dabn)Ni(C$_4$H$_6$)] were identified by high-resolution NMR, but further weak diamine signals were detected. At present the dissociation equilibrium is tentatively described by the equation: 2{(diamine)Ni(η^2-C$_4$H$_6$)}$_2$(μ-η^2,η^2-C$_4$H$_6$) → 3(diamine)Ni(η^2-C$_4$H$_6$)$_2$ + [(diamine)Ni]. It is tempting to suggest that the species [(diamine)Ni] may be a dimer [(diamine)Ni=Ni(diamine)] with a d^{10}(Ni)−d^{10}(Ni) bond.
(40) Hobgood, R. T.; Goldstein, J. H. *J. Mol. Spectrosc.* **1964**, *12*, 76.
(41) Paiaro, G. *Organomet. Chem. Rev. Sect. A* **1970**, *6*, 319.

at significantly lower wave number (1560 cm^{-1}) than those of analogous bis(phosphane)nickel(0)−ethyne complexes, e.g., (^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Ni(C$_2$H$_2$) (1598 cm^{-1})[42] (Table 2). In the ^{1}H and ^{13}C NMR spectra (−80 °C) of **3**, the dabn ligand (Table 1) gives rise to five proton and four carbon signals, which are (on average) at slightly lower field than those observed for the (dabn)Ni(0)−ethene complex **1**. The ethyne ligand displays signals at δ(H) 4.65 and δ(C) 118.7 with a coupling constant of ^1J(CH) = 178 Hz. In order to assess the information the ethyne resonances provide, one has to recall that for mononuclear bis(phosphane)nickel(0)−ethyne complexes, e.g., (^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Ni(C$_2$H$_2$) [δ(H) 7.29; δ(C) 123.8; ^1J(CH) = 202 Hz],[42] the ^{1}H and ^{13}C resonances are at low field relative to those of uncoordinated ethyne (Table 2). This shift is reversed[43] for dinuclear complexes in which ethyne is ligated by two nickel(0) moieties, e.g., {(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Ni}$_2$(μ-C$_2$H$_2$) [δ(H) 5.52; δ(C) 86.3; ^1J(CH) = 188 Hz].[42] The coupling constant ^1J(CH) = 249 Hz, as attributed to uncoordinated ethyne, decreases to about 200 Hz upon complexation of the ethyne molecule to a single bis(phosphane)nickel(0) moiety (as verified by us for more than 30 compounds). A further, moderate reduction down to 187 Hz is observed only when the ethyne molecule is ligated to two bis(phosphane)nickel(0) moieties (verified by us for approximately 10 compounds).[43] Thus, although the ^{1}H and ^{13}C chemical shifts observed for the ethyne ligand in complex **3** appear to be unexceptional, the coupling constant ^1J(CH) = 178 Hz is extremely low and is by far the smallest for any known Ni(0)−ethyne complex (Table 2). We conclude from the IR and NMR data that, in complex **3**, *TP*-3 Ni(0) is coordinated by the dabn N atoms and one ethyne ligand and that an exceedingly large charge transfer from Ni(0) into an antibonding orbital of the ethyne ligand occurs.

(C$_9$H$_{18}$N$_2$)Ni(CO)$_2$ (4). Complexes **1**−**3** react with CO (−30 °C) by the exchange of all ligands to give Ni(CO)$_4$. This raised the question as to whether complex **4**, which is conceived as an intermediate in these reactions, is stable or not. When the neat colorless liquids of Ni(CO)$_4$ (in excess) and dabn are mixed at 20 °C, the mixture changes color to orange and CO is evolved. After a short period, pure microcrystalline orange needles of the (dabn)Ni(0)−CO complex **4** separate (85%) (eq 5). On the other hand, when **4** is exposed to CO at −30 °C the dabn ligand is readily displaced to form Ni(CO)$_4$.
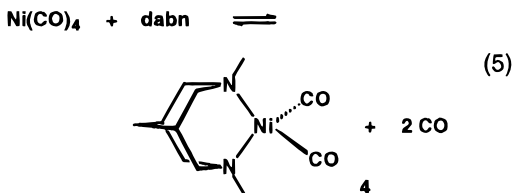
As expected, complex **4** is thermally more stable than the Ni(0)−alkene complexes **1**−**3**. The solid may be kept indefinitely at 20 °C. When the complex is heated to 50 °C, the color slowly changes to red, but a rapid decomposition of the crystals takes place only at 130 °C. Also, under the conditions of the

mass spectrometer (EI, 70 eV, 50 °C), the complex vaporizes without decomposition. In the spectrum, the molecular ion (268, 1%) is detected and 2-fold loss of CO affords the base peak [(dabn)Ni]$^+$ (212).

For dissolved **4**, the ^{1}H and ^{13}C NMR data of the dabn ligand (Table 1) resemble those of the (dabn)Ni(0) complexes **1**−**3**. The ^{13}C resonance of the CO ligand is found at δ = 196.0, which is, surprisingly, not much different from that of Ni(CO)$_4$.[44,45] In the IR spectrum of **4** (pentane), two strong ν(CO) bands are observed at 1984 (A$_1$) and 1896 cm^{-1} (B$_1$), which are at a lower wave number than for other L$_2$Ni-(CO)$_2$ complexes [e.g., (^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Ni(CO)$_2$ 1994, 1935 cm^{-1}].[35]

Thus, we conclude that in complex **4** a *T*-4 Ni(0) center is coordinated by dabn and two CO ligands. The structure of **4** is related to those of the (dabn)Ni(0)−butadiene complexes **2** and **2a**. Complex **4** may be considered as the first well-characterized complex of the type (diamine)Ni(CO)$_2$, particularly since (NH$_3$)$_2$Ni(CO)$_2$ has not been isolated in a pure form (see the Introduction) and the hypothetical [(tmeda)Ni(CO)$_2$] is not accessible in a similar reaction.[6]

Discussion

The aim of this work was to prepare (diamine)Ni(0)−ethene and −ethyne complexes, and this was eventually achieved using the bicyclic diamine, *N,N′*-dimethyl-3,7-diazabicyclo-[3.3.1]nonane (dabn). In this paper, we describe our search for a suitable ligand and the preparation and properties of four novel (diamine)Ni(0) complexes containing ethene (**1**), butadiene (**2**, **2a**), ethyne (**3**), and CO (**4**) using this ligand. Prior to this study, no (diamine)Ni(0) complex with ethene and ethyne as the parent alkene and alkyne was known. It was also found that the dabn complexes **2** and **2a** (dec. 20 °C) containing butadiene are markedly more stable than the already known tmeda derivatives (dec. −40 °C). Similarly, the rather stable CO complex **4** (dec. 130 °C) was preceded only by reports of the highly labile and poorly characterized (NH$_3$)$_2$Ni(CO)$_2$ (dec. −60 °C). All previous attempts to prepare complexes such as (tmeda)Ni(C$_2$H$_4$), (tmeda)Ni(C$_2$H$_2$), and (tmeda)Ni(CO)$_2$ have been unsuccessful.

Dabn is currently unique among hard chelating diamine ligands in its ability to ligate the soft Ni(0) in combination not only with stronger π-acceptors but also with nonactivated alkenes or alkynes. Preliminary studies have shown that neither the bispidine derivatives 3,7-diazabicyclo[3.3.1]nonan-9-one nor the commercially available (−)-sparteine coordinate to the [Ni(0)(C$_2$H$_4$)] fragment. (−)-Sparteine, which forms stable complexes with metal *ions*,[46] prefers the chair/boat conformation,[47] and this conformation must be converted into a chair/chair conformation before chelating coordination is possible. It would appear that the energy required for this conformational change is too large to be compensated by the energy gained upon forming two N→Ni(0)(C$_2$H$_4$) coordinative bonds. Perhaps we should mention here that we have not yet tried the symmetrical α-isosparteine, which is a stronger binding ligand than (−)-sparteine due to its rigid chair/chair conformation.[48,49]

(42) Pörschke, K.-R. *Angew. Chem.* **1987**, *99*, 1321; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1288.

(43) The changes in the chemical shift may be explained by a formal change in the hybridization of the ethyne carbon atoms sp → sp^2 → sp^3 upon coordination of the triple bond to one and two nickel atoms, respectively. Thus, in the first instance, the protons and carbon atoms become olefinic due to the limiting structure of a metallacyclopropene (downfield shift), while upon formal coordination of this metallacyclopropene to a second metal center (limiting structure of a dimetallabicyclobutane) they become aliphatic (upfield shift). The steady decrease of the coupling constant is also in agreement with the anticipated change in hybridization (hydrocarbons: sp, 249 Hz; sp^2, 156 Hz; sp^3, 125 Hz).[33]

(44) The ^{13}C NMR signal of Ni(CO)$_4$ is at δ 191.6. For L−Ni(CO)$_3$ and L$_2$Ni(CO)$_2$ complexes, the resonance of the carbon monoxide ligand is shifted to lower field, and the magnitude of the low-field shift generally follows the donor strength of the ligand L; e.g., (Me$_3$P)Ni(CO)$_3$: 196.6,[44a] Li$^+$[CH$_3$−Ni(CO)$_3$]$^-$: 209.5,[44b] (^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Ni(CO)$_2$: 204.8.[35] (a) Bodner, G. M. *Inorg. Chem.* **1975**, *14*, 1932. (b) Kleimann, W.; Pörschke, K.-R.; Wilke, G. *Chem. Ber.* **1985**, *118*, 323 and literature cited therein.

(45) The changes in the ligand NMR data of *T*-4 Ni(0) complexes can be relatively small. This is due to the fact that back-bonding from Ni(0) into acceptor orbitals on the π-ligand is significantly smaller than for *TP*-3 Ni(0) complexes. Pörschke, K.-R.; Mynott, R.; Krüger, C.; Romao, M. J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39*, 1076.

One feature favoring coordination of the dabn ligand to Ni(0) is the arrangement of the donor N atoms in the molecule. Not only is the diamine structurally preorganized but the N atoms are also ideally prepositioned for coordination to the metal.[50] The principles of preorganization and prepositioning are essential components of the well-developed concept of the macrocyclic effect.[51,52] Moreover, the species formed when dabn is bound to Ni(0) is structurally highly organized. Coordination of dabn to the Ni(0) center results in the formation of two additional six-membered rings and turns the dabn molecule with its semi adamantane type structure into one with a rigid full adamantane type structural motif.[53]

In order to assess the influence dabn exerts to Ni(0) relative to other donor ligands, it is instructive to look at the properties of the coligated π-acceptor ligands. In the *T*-4 (dabn)Ni(0)-*butadiene* complexes, the electronic influence of bicyclic dabn is similar to that of open-chain tmeda, which only coordinates to Ni(0) in combination with π-ligands of moderate (e.g., butadiene) to high acceptor strength. No assessment of the donor strength of tmeda has so far been made, and there are no phosphane complexes of the type $(R_2PC_2H_4PR_2)Ni(\eta^2\text{-}C_4H_6)_2$ known to which **2a** and $(tmeda)Ni(\eta^2\text{-}C_4H_6)_2$ could be compared. For the *T*-4 (dabn)Ni(0)-*carbonmonoxide* complex **4**, the NMR CO resonance [$\delta(C)$ 196.0] is almost of the same magnitude as for $Ni(CO)_4$, and it occurs at a much higher field than expected ($\sim$210).[44] No reasonable explanation can be given at present. In contrast, in the IR spectrum of **4** the CO stretching absorptions appear at very low wave numbers, indicating a high degree of back-bonding from Ni(0) to the acceptor ligand. This effect is even stronger in the *TP*-3 (dabn)Ni(0)-*ethene* and −*ethyne* complexes **1** and **3** (see Table 2). For both compounds the C−H, C=C, and C≡C stretching vibrations occur at lower wave numbers than for any other common Ni(0)−ethene or −ethyne complex. Furthermore, in the NMR spectra, the ethene ligand protons and carbon atoms

of **1** are strongly shielded [$\delta(H)$ 0.27; $\delta(C)$ 20.4], and the resonances almost correspond to those expected for a saturated hydrocarbon. The effect on the chemical shift is less obvious for the ethyne protons and carbon atoms of **3**, but for both ethene and ethyne ligands the coupling constants of $^1J(CH) = 142$ Hz (**1**) and 178 Hz (**3**) are exceptionally low.

These findings indicate that the dabn ligand coordinated to Ni(0) induces an exceedingly strong charge transfer from Ni(0) into an antibonding π-ligand orbital.[54] According to the IR and NMR data, the charge transfer induced is markedly stronger for the dabn ligand than for a diphosphane ligand or for bpy[37b] (and even more so than for phosphite type and 1,4-diazabutadiene ligands). The donor effect of the dabn ligand is intermediate between that of diphosphane (or bpy) ligands and carbanionic ligands (Table 2), of which the latter represent the strongest donor ligands known.[55]

The very large ligand effect of the diamine toward Ni(0), observed spectroscopically for complexes **1**, **3**, and **4**, is consistent with *ab initio* MO-SCF calculations on the hypothetical amine and phosphane *TP*-3 Ni(0)−ethene complexes $(H_3N)_2Ni(C_2H_4)$ and $(H_3P)_2Ni(C_2H_4)$.[8] These indicate a charge distribution in $(H_3N)_2Ni(C_2H_4)$ of +0.11 e (NH_3), +0.58 e (Ni), −0.78 e $(C_2H_4$; calculated C=C bond length 1.45 Å), and in $(H_3P)_2Ni(C_2H_4)$ of +0.07 e (PH_3), +0.35 e (Ni), −0.48 e $(C_2H_4$; the calculated C=C bond length of 1.41 Å agrees well with experimental data). The data confirms that the hard amine is a stronger donor toward Ni(0) than the soft phosphane, which can also act as an acceptor. Furthermore, the data show that, although in both compounds the negative charge on the ethene ligand is mainly compensated by the positive charge at the nickel center, the polarization of the Ni(0)−C_2H_4 coordinative bond is considerably larger in $(H_3N)_2Ni(C_2H_4)$ than in $(H_3P)_2Ni(C_2H_4)$. In terms of the Pearson HSAB concept, the hard amine ligand forces the soft nickel atom to transfer charge to the π-ligand, causing Ni(0) to become less soft and hence able to coordinate the hard amine ligand more strongly.[56]

Conclusion

Hancock and Martell have predicted that *high levels of preorganization are not confined to macrocycles or cryptates and can just as easily occur in chelating ligands,*[52b] but no experimental evidence was given. Our study has verified this presumption, since the coordination of a diamine to the $[Ni(0)(C_2H_4)]$ fragment is possible only when the principles of preorganization (ligand) and prepositioning (donor atoms) are applied to the diamine ligand. These principles, which were developed from studies with macrocyclic ligands and thus are collectively known as macrocyclic effect, are—as shown here—also valid for common and medium-sized rings and bi- or multicyclic ring systems.[57] The denotation macrocyclic effect with its implication of large rings is therefore too narrow an expression, and since it is the position of the donor atoms and

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(47) Bohlmann, F.; Zeisberg, R. *Chem. Ber.* **1975**, *108*, 1043 and literature cited therein.

(48) Przybylska, M.; Barnes, W. H. *Acta Crystallogr.* **1953**, *6*, 377.

(49) For Mg, see: Kageyama, H.; Miki, K.; Kai, Y.; Kasai, N.; Okamoto, Y.; Yuki, H. *Acta Crystallogr. B* **1982**, *38*, 2264. Okamoto, Y.; Suzuki, K.; Kitayama, T.; Yuki, H.; Kageyama, H.; Miki, K.; Tanaka, N.; Kasai, N. *J. Am. Chem. Soc.* **1982**, *104*, 4618.

(50) A change in the hybridization of the donor upon complex formation must be taken into account when choosing an optimal geometry for a potential ligand.

(51) (a) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 6540. (b) Hinz, F. P.; Margerum, D. W. *J. Am. Chem. Soc.* **1974**, *96*, 4993; *Inorg. Chem.* **1974**, *13*, 2941.

(52) (a) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271. (b) Hancock, R. D.; Martell, A. E. *Comments Inorg. Chem.* **1988**, *6*, 237 and literature cited therein.

(53) Although illustrative, this fact alone does not explain the stability of the complexes because both (−)-sparteine and *N,N′*-dimethyl-3,7-diazabicyclo[3.3.1]nonan-9-one fail to form a nickel(0)−ethene complex. The stability of complexes **1**−**4** is based on the optimal geometry of free dabn, which is superior to that of the above-mentioned reference diamines with a bispidine skeleton (leaving α-isosparteine out of consideration). It is, however, conceivable that a different bicyclic or multicyclic structure would also give a satisfactory arrangement of the N atoms.

(54) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, C71. (b) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783. (c) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(55) (a) Pörschke, K.-R.; Jonas, K.; Wilke, G. *Chem. Ber.* **1988**, *121*, 1913. (b) Jonas, K.; Krüger, C. *Angew. Chem.* **1980**, *92*, 513; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520. Jonas, K. *Adv. Organomet. Chem.* **1981**, *19*, 97 and literature cited therein.

(56) For a detailed treatment of this matter, see: Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734.

(57) (a) Examples of common and medium-sized rings in coordination chemistry: 1,5-cyclooctadiene (cod), 1,4,7-triazacyclononane, 1,5,9-cyclododecatriene isomers. Example of bicyclic rings: norbornadiene. Examples of multicyclic rings: sparteine, α-isosparteine. (b) Earlier we used the term macrocyclic effect to explain the stability of certain cod complexes[36] and the term cyclic effect with reference to Ni(cdt).[35]

the direction of the lone-pairs which is important, we would suggest that the term *prepositioning effect* is a more suitable alternative.

In view of the interesting ligand properties of dabn reported here (increased binding and electron donation), we expect that dabn and related molecules will lead to novel complexes with unusual stability and metals with unusual oxidation states.[58]

Experimental Section

The complexes were handled under an atmosphere of argon with Schlenk type glassware in order to exclude oxygen and moisture. Microanalyses were performed by Microanalytisches Labor Dornis und Kolbe, Mülheim. ^{1}H NMR spectra were recorded at 80, 200, and 400 MHz and ^{13}C NMR spectra were at 50.3, 75.5, and 100.6 MHz on Bruker WP-80, AM-200, AX-300, and WH-400 instruments (relative to internal tetramethylsilane). For the NMR spectra, solutions of the compounds in THF-d_8 were used unless otherwise indicated. Solutions of thermolabile complexes were prepared under an argon atmosphere at the temperature at which the spectra were recorded. IR spectra were taken on a Nicolet 7199 FT-IR system, Raman were on a Coderg-LRT 800 instrument (excitation: argon lines at 488.0 and 514.5 nm), and EI mass spectra were on a Finnigan MAT 8200. Ni(C$_2$H$_4$)$_3$[2] was prepared from Ni(cdt),[31] as published (cdt = *trans,trans,trans*-1,5,9-cyclododecatriene).

N,N'-Dimethyl-3,7-diazabicyclo[3.3.1]nonan-9-one. The synthesis was carried out according to the published procedure[24] but on a pilot-plant scale (30 L reaction vessel) because of the poor yield: 1-methyl-4-piperidone (12 mol; Aldrich), *N*-methylamine (12 mol; Fluka), paraformaldehyde (24 mol), acetic acid (24 mol), methanol (20 L); concentric tube column rectification; yield 60 g (3%); colorless solid; mp 44 °C; bp 53 °C (0.07 mbar); C$_9$H$_{16}$N$_2$O (168.2) [14789-54-9]. IR (neat or THF): 1740, 1706 cm^{-1} (ν C=O). Raman: 1734, 1713 cm^{-1} (ν C=O). EI-MS (70 eV, 40 °C): *m/e* (%) 168 (M$^+$, 14), 58 ([Me$_2$N=CH$_2$]$^+$, 100), 42 ([H$_2$C=N=CH$_2$]$^+$, 69). ^{1}H NMR (400 MHz, 27 °C): δ 2.95 (dd, 4H, H$_{eq}$), 2.69 (dd, 4H, H$_{ax}$), 2.39 (m, 2H, C$_{tert}$H), 2.22 (s, 6H, CH$_3$). ^{13}C NMR (50.3 MHz, 27 °C): δ 211.7 (1C, C=O), 61.3 (4C, CH$_2$), 47.1 (2C, C$_{tert}$H), 44.8 (2C, NCH$_3$).

1-(Methoxymethyl)-N,N'-dimethyl-3,7-diazabicyclo[3.3.1]nonan-9-one. The substance is a byproduct of the synthesis described above (not mentioned in ref 24); yield 56 g (2.2%); C$_{11}$H$_{20}$N$_2$O$_2$ (212.3); bp 62 °C (0.07 mbar). IR (neat): 1730 (ν C=O), 1110 cm^{-1} (CH$_2$OCH$_3$). EI-MS (70 eV, 40 °C): *m/e* (%) 212 (M$^+$, 20), 58 ([Me$_2$N=CH$_2$]$^+$, 100), 42 ([H$_2$C=N=CH$_2$]$^+$, 25). ^{1}H NMR (200 MHz, CDCl$_3$, 27 °C): δ 3.39 (2H, CH$_2$O), 3.31 (3H, OCH$_3$), 2.27 (6H, NCH$_3$), 3.10, 2.97, 2.74, 2.50 (each dd, 2H, NCH$_a$H$_b$ and NC'H$_a$H$_b$), 2.54 (m, 1H, C$_{tert}$H). ^{13}C NMR (50.3 MHz, CDCl$_3$, 27 °C): δ 213.9 (1C, C=O), 74.4 (1C, CH$_2$O), 60.8, 64.0 (each 2C, NCH$_2$ and NC'H$_2$), 59.4 (1C, OCH$_3$), 50.1 (1C, C$_{quat}$), 46.5 (1C, C$_{tert}$H), 44.9 (2C, NCH$_3$).

N,N'-Dimethyl-3,7-diazabicyclo[3.3.1]nonane. The compound was synthesized as published[24] from N,N'-dimethyl-3,7-diazabicyclo[3.3.1]-nonan-9-one (30 g, 180 mmol); concentric tube column rectification; yield 16.5 g (60%); C$_9$H$_{18}$N$_2$ (154.2) [14789-33-4]; bp 54 °C (28 mbar); n_D^{20} = 1.4902. EI-MS (70 eV, 40 °C): *m/e* (%) 154 (M$^+$, 23), 124 ([M − 2CH$_3$]$^+$, 16), 58 ([Me$_2$N=CH$_2$]$^+$, 77), 42 ([H$_2$C=N=CH$_2$]$^+$, 100). For [1]H (400 MHz, 27 °C) and [13]C (50.3 MHz, 27 °C) NMR data, see Table 1.

(C$_9$H$_{18}$N$_2$)Ni(C$_2$H$_4$) (1). To a solution of Ni(C$_2$H$_4$)$_3$, prepared from Ni(cdt) (466 mg, 2.00 mmol) and ethene in diethyl ether (20 mL) at 0 °C, is added a solution of dabn (0.4 mL; excess) in diethyl ether (10 mL) at −10 °C. Over the course of 30 min, a yellow microcrystalline precipitate forms. At −30 °C the product is separated from the mother

liquor by means of a capillary, washed twice with pentane, and dried in vacuo; yield 400 mg (83%). The solid decomposes rapidly at 50 °C and slowly at 0 °C (decoloration to grey). The complex is very sensitive to oxygen. IR (KBr): 2990, 2980 (ν C−H), 1510 [ν(C=C) + δ_s(CH$_2$)], 1115 (ρ_w CH$_2$), 865 cm^{-1} (ρ_r CH$_2$). EI-MS (70 eV, 50 °C): *m/e* (%) 240 (M$^+$, <1), 212 ([M − C$_2$H$_4$]$^+$, <1), 154 ([dabn]$^+$, 90), 58 ([Me$_2$N=CH$_2$]$^+$, 100), 42 ([H$_2$C=N=CH$_2$]$^+$, 40). ^{1}H NMR (400 MHz, −30 °C): δ 0.27 (s, 4H, C$_2$H$_4$); for dabn resonances see Table 1. ^{13}C NMR (100.6 MHz, −30 °C): δ 20.4 (2C, ^1J(CH) = 142 Hz, C$_2$H$_4$); for dabn resonances see Table 1. Anal. Calcd for C$_{11}$H$_{22}$N$_2$Ni (241.0): C, 54.82; H, 9.20; N, 11.62; Ni, 24.36. Found: C, 54.81; H, 9.24; N, 11.68; Ni, 24.31.

{(C$_9$H$_{18}$N$_2$)Ni(η^2-C$_4$H$_6$)}$_2$(μ-C$_4$H$_6$) (2). Butadiene (2 mL) was added to a suspension of **1** (482 mg, 2.00 mmol) in diethyl ether (20 mL) at −40 °C. The color of the mixture changed to red, and the mixture was stirred at −40 °C until all **1** was dissolved. The solution was briefly warmed to 20 °C, and pentane (20 mL) was added. In the course of 12 h, dark red crystals separated at −78 °C. The product was recrystallized from diethyl ether/pentane and dried under vacuum at −30 °C; yield 310 mg (53%). IR (KBr): 3065, 2995 (ν C−H), 1580 (ν C=C, uncoordinated), 1190, 655 cm^{-1}. EI-MS (70 eV, 0 °C): *m/e* (%) 266 ([(dabn)Ni(C$_4$H$_6$)]$^+$, <1), 212 ([(dabn)Ni]$^+$, 2), 154 ([dabn]$^+$, 100), 58 ([Me$_2$N=CH$_2$]$^+$, 30). For ^{1}H and ^{13}C NMR data, see that for **2a**. Anal. Calcd for C$_{30}$H$_{54}$N$_4$Ni$_2$ (588.2): C, 61.26; H, 9.25; N, 9.52; Ni, 19.96. Found: C, 61.35; H, 9.26; N, 9.48; Ni, 19.88.

(C$_9$H$_{18}$N$_2$)Ni(η^2-C$_4$H$_6$) (2a). This complex was observed when **2** was dissolved in THF-d_8. ^{1}H NMR (400 MHz, −80 °C) δ 5.49 (m, 2H, =CH−$_{uncoord}$), 4.80 (dd, 2H, =CH$_Z$H$_{uncoord}$), 4.52 (dd, 2H, =CHH$_{E\text{-,uncoord}}$), 3.45 (m, 2H, =CH−$_{coord}$), 1.87 (d, 2H, =CHH$_{E,coord}$), 1.59 (d, 2H, =CH$_Z$H$_{coord}$); for dabn resonances see Table 1. The assignment of the butadiene proton signals is in accordance with a COSY 2D-NMR experiment. ^{13}C NMR (100.6 MHz, −80 °C): δ 145.6 (2C, −CH=$_{uncoord}$), 97.9 (2C, =CH$_{2,uncoord}$), 62.2 (2C, −CH=$_{coord}$), 48.8 (2C, =CH$_{2,coord}$); for dabn resonances see Table 1.

(C$_9$H$_{18}$N$_2$)Ni(C$_2$H$_2$) (3). A red suspension of **2** (588 mg, 1.00 mmol) in diethyl ether (10 mL) was exposed to ethyne (48 mL, 2 mmol) at −78 °C. Within a few minutes, the suspension turned yellow. The precipitate was isolated from the mother liquor, washed twice with pentane at −78 °C, and dried under vacuum at −78 °C; yield 200 mg (42%); dec. as a solid >−30 °C, dissolved >−60 °C (THF). IR (KBr, −80 °C): 3010, 2980 (ν ≡CH), 1560 (ν C≡C), 900, 630 cm^{-1} (γCCH). ^{1}H NMR (200 MHz, −80 °C): δ 4.65 (s, 2H, C$_2$H$_2$); for dabn resonances, see Table 1. ^{13}C NMR (75.5 MHz, −80 °C): δ 118.7 (2C, ^1J(CH) = 178 Hz, C$_2$H$_2$); for dabn resonances, see Table 1. Anal. Calcd for C$_{11}$H$_{20}$N$_2$Ni (239.0): C, 55.28; H, 8.44; N, 11.72; Ni, 24.56. Found: C, 55.20; H, 8.78; N, 11.60; Ni, 24.51.

(C$_9$H$_{18}$N$_2$)Ni(CO)$_2$ (4). Ni(CO)$_4$ (1.0 g, excess) was mixed with dabn (771 mg, 5.00 mmol) at 20 °C in the absence of a solvent. CO evolved from the initially colorless mixture, and an orange crystalline product was formed within 1 h. Excess Ni(CO)$_4$ was evaporated under vacuum to afford the analytically pure product; yield 1.14 g (85%). EI-MS (70 eV, 50 °C): *m/e* (%) 268 (M$^+$, 1), 240 ([M − CO]$^+$, 48), 212 ([M − 2CO]$^+$, 100), 154 ([dabn]$^+$, 24). IR: (pentane) 1984 (CO, A$_1$), 1896 cm^{-1} (B$_1$); (THF) 1971, 1879 cm^{-1}; (KBr) 1970, 1880 cm^{-1} (broad). For [1]H (400 MHz, 27 °C) and [13]C (50.3 MHz, 27 °C) NMR data, see the text and Table 1. Anal. Calcd for C$_{11}$H$_{18}$N$_2$NiO$_2$ (269.0): C, 49.12; H, 6.75; N, 10.42; Ni, 21.82. Found: C, 49.07; H, 6.78; N, 10.46; Ni, 21.69.

(58) Since the reaction used to prepare dabn only has a yield of ~2%, we would welcome a more efficient synthesis of dabn.

(59) Michaelis, S. Ph.D. Dissertation, Universität Bochum, 1991.