4724 *Organometallics* **1998,** *17,* 4724−4733

# Reassessment of the Electronic and Molecular Structure, Bonding, and Stability of Zerovalent Nickel Acetylene Complexes by the Density Functional Method

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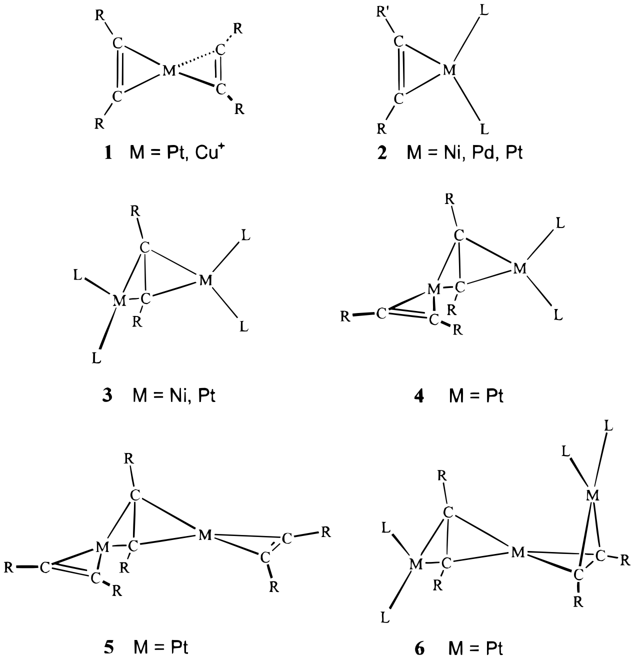
*Received March 9, 1998*

The density functional theory (DFT) method has been used to study the electronic and molecular structure of mono-, di-, and trinuclear zerovalent nickel complexes containing acetylene and $\sigma$-donor ligands. The calculations were carried out for the model compounds $(C_2H_2)_2Ni$ (**10**) and $(C_2H_2)Ni(PH_3)_2$ (**12**) with quasi-tetrahedral (**10a**, **12a**) and planar (**10b**, **12b**) conformations as well as for $(C_2H_2)_3Ni_2$ (**14**) and $(C_2H_2)_4Ni_3$ (**23**). Rotational preference of complexes **10** and **12** is discussed on the basis of the 18 VE rule, relative energies, and natural bond orbital (NBO) population analyses. Optimized geometries and calculated IR and NMR properties are compared with known experimental data. It is shown how the effective back-bonding into acetylene in-plane $\pi_{\|}$* MO(s) accounts for rotational preference of **10** and **12** as well as for the main features of molecular geometry of polynuclear Ni(0) compounds. Binding energies (BEs) of acetylene in **10a** and **12b** are calculated at the DFT, HF, MP2−MP4, CCSD, and CCSD(T) levels and compared to those of ethylene in $(C_2H_4)_2Ni$ (**17**), $(C_2H_4)Ni(C_2H_2)$ (**18**), and $(C_2H_4)Ni(PH_3)_2$ (**19**) as well as to those of CO in $Ni(CO)_x$, $x =$ 4 (**20**), 3 (**21**), 2 (**22**). It turns out that with respect to **10a** the bridging acetylene of **14** is bound almost 2 times stronger. Calculated BEs together with energies of association reactions $L' + NiL_2 \rightarrow NiL_2L'$ (L, L′ = CO, $PH_3$, $C_2H_2$) and $L + NiL_3 \rightarrow NiL_4$ (L = CO, $PF_3$, $PMe_3$, $PH_3$, $C_2H_2$) as well as of the exchange reaction $Ni(CO)_4 + 2C_2H_2 \rightarrow Ni(C_2H_2)_2 + 4CO$ are used in the discussion of thermodynamic and kinetic stability of the formally two-coordinated bis(alkyne)Ni compounds.

## Introduction

The organometallic aspect of the coordination of alkynes to transition metals has long been of interest. This can be attributed to use of some of these compounds in catalytic processes such as hydrogenation, polymerization, cyclization, and metathesis reactions.[1] The essential qualitative understanding of the rich alkyne transition metal chemistry is inherently connected with the Dewar−Chatt−Duncanson model,[2] i.e., with the ability of alkynes to act as donor and acceptor ligands. While donor−acceptor interactions of ligands with transition metals are most widespread in organometallic chemistry, alkynes exhibit a remarkable flexibility of coordination modes, being able to occupy up to four coordination sites. A variety of alkyne complexes with $d^{10}$ metals represented by **1**−**6** (Scheme 1) has been known for long.[3−6]

### Scheme 1



**1** M = Pt, Cu$^+$

**2** M = Ni, Pd, Pt

**3** M = Ni, Pt

**4** M = Pt

**5** M = Pt

**6** M = Pt

The substituents R in complexes **1**−**6** are alkyl-, phenyl-, Si-, or O-containing groups. The ligands L are two-electron donors such as trialkyl, triphenylphosphines, or a cycloocta-1,5-diene.[3−6] In complexes **1**−**6** two alkyne ligands bind to the $d^{10}$ metal in quasi-tetrahedral arrangement, while two $\sigma$ donors and one alkyne prefer a planar conformation. On the basis of a

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(1) Wilke, G. *Angew. Chem.* **1988**, *100*, 189; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185, and references therein.

(2) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2929.

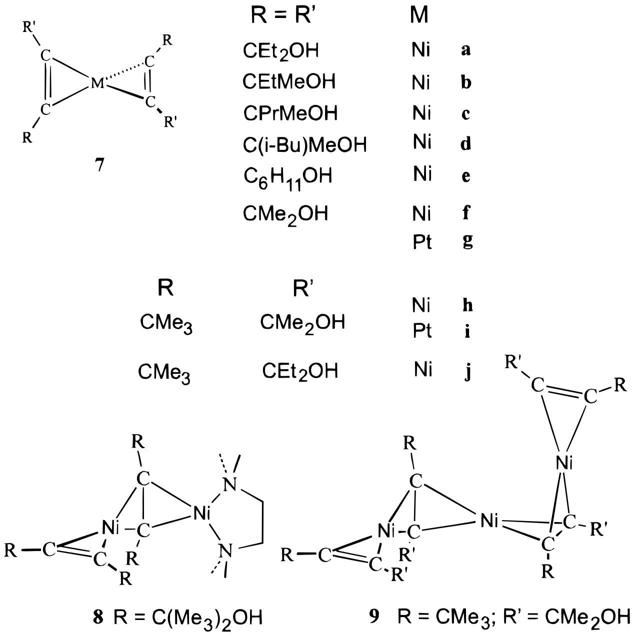
S0276-7333(98)00175-7 CCC: $15.00
Publication on Web 09/12/1998

number of semiempirical[7,8] and ab initio[9,10] MO calculations on the model compounds of **1** and **2**, back-bonding interaction of the metal d electrons with the empty alkyne $\pi^*$ orbitals has been known to account for the stability and molecular geometry of these compounds. However, to our knowledge an explicit quantitative comparison of the bonding in complexes **1** and **2** has not been reported so far. Since the complexes **1** and **2** can be regarded as the basic molecular units of the di- and trinuclear complexes **3**−**6**, such a comparison may contribute to the understanding of the bonding in polynuclear compounds.

The recent synthesis of the mono-, di-, and trinuclear Ni complexes **7**−**9**[11] revived our interest in bonding properties of these species (Scheme 2).

Complex **9** is the only trinuclear homoleptic alkyne complex of d$^{10}$-metals known to date. In this paper we present and discuss the result of density functional theory (DFT) calculations on the model compounds of mono-, di-, and trinuclear complexes **2**, **5** (M = Ni), and **7**−**9**. Our study focuses on molecular and electronic structure, charge transfer, and bond energies as well as on IR and NMR spectra. As a convenient starting point for our discussion, we present a simple qualitative outline of the electronic structure of the model compounds **10a**, **10b**, **12a**, and **12b** (Scheme 3).

**Scheme 2**



In the following sections we discuss the DFT fully optimized geometries of the model compounds **10**, **12**, and $Ni_2(C_2H_2)_3$ (**14**) as well as of the free ligands RC≡CR, R=H (**15**), CEt$_2$OH (**15a**), and $PH_3$ (**16**). Calculated IR and NMR properties are compared with available experimental data. Calculated binding energies of acetylene are compared with those of ethylene for analogous model compounds $Ni(C_2H_4)_2$ (**17**), $Ni(C_2H_2)(C_2H_4)$ (**18**), and $Ni(C_2H_4)(PH_3)_2$ (**19**). To test thermodynamically the postulated isolobal relationship of an acetylene with two two-electron ligands,[7g] we compare the binding energy (BE) of acetylene with those of carbon monoxide in nickel carbonyls $Ni(CO)_x$, $x$ = 4 (**20**), 3 (**21**), and 2 (**22**). Donor−acceptor interactions are quantified by means of the natural bond orbital (NBO) population analysis. We show how the structural

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(3) (a) Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* **1971**, *93*, 3797. (b) Robertson, G. B.; Whimp, P. O. *J. Organomet. Chem.* **1971**, *32*, C69. (c) Davies, B. W.; Payne, N. C. *Inorg. Chem.* **1974**, *13*, 1848. (d) Dubey, R. J. *Acta Crystallogr.* **1975**, *B31*, 1860. (e) Davies, B. W.; Payne, N. C. *J. Organomet. Chem.* **1975**, *99*, 315. (f) Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1976**, 759. (g) Smart, L. E.; Browning, J.; Green, M.; Laguna, A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1777. (h) Manojlovic-Muir, L.; Muir, K. W.; Walker R. *Acta Crystallogr.* **1979**, *B35*, 2416. (i) Boag, N. M.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stansfield, R. F. D.; Thomas, M. D. O.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 2182. (j) Boag, N. M.; Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2170. (k) Farrar, D. H.; Payne, N. C. *Inorg. Chem.* **1981**, *20*, 821. (l) Farrar, D. H.; Payne, N. C. *J. Organomet. Chem.* **1981**, *220*, 251. (m) Stone, F. G. A. *Acc. Chem. Res.* **1981**, *14*, 318. (n) Boag, N. M.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1981**, 862. (o) Burckett-St. Laurent, J. C. T. R.; Hitchcock, P. B.; Kroto, H. W.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1141. (p) Green, M.; Howard, J. A. K.; Pain, G. N.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1327. (q) Packet, D. L.; Syed, A.; Trogler, W. C. *Organometallics* **1988**, *7*, 159. (r) Komatsu, K.; Kamo, H.; Tsuji, R.; Masuda, H.; Takeuchi, K. *J. Chem. Soc., Chem. Commun.* **1991**, 71. (s) Lu, Z.; Abboud, K. A.; Jones, W. M. *Organometallics* **1993**, *12*, 1471. (t) Sünkel, K.; Birk, U.; Robl, Ch. *Organometallics* **1994**, *13*, 1679.

(4) (a) Dickson, R. S.; Ibers, J. A. *J. Organomet. Chem.* **1972**, *36*, 191. (b) Day, V. W.; Abdel-Mequid, S. S.; Dabestani, S.; Thamas, M. G.; Pretzer, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 8289. (c) Muetterties, E. L.; Pretzer, W. R.; Thomas, M. G.; Beier, B. F.; Thorn, D. L.; Day, V. W.; Anderson, A. B. *J. Am. Chem. Soc.* **1978**, *100*, 2090. (d) Diercks, R.; Kopf, J.; Dieck, H. T. *Acta Crystallogr.* **1984**, *C40*, 363. (e) Pörschke, K. R.; Mynott, R.; Angermund, K.; Krüger, C. *Z. Naturforsch.* **1985**, *40b*, 199. (f) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992. (g) Pörschke, K. R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1985**, *97*, 334; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 323. (h) Rosenthal, U.; Schulz, W.; Görls, H. *Z. Anorg. Allg. Chem.* **1987**, *550*, 169. (i) Bonrath, W.; Pörschke, K. R.; Wilke, G., Angermund, K.; Krüger, C. *Angew. Chem.* **1988**, *100*, 853; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 833 (j) Rosenthal, U.; Oehme, G.; Görls, H.; Burlakov, V. V.; Polyakov, A. V.; Janowsky, A. I.; Struchkov, Yu. T. *J. Organomet. Chem.* **1990**, *389*, *409*; **1990**, *390*, 113. (k) Bartik, T.; Happ, B.; Iglewsky, M.; Bandmann, H.; Boese, R.; Heimbach, P.; Hoffmann, T.; Wenschuh, E. *Organometallics* **1992**, *11*, 1235. (l) Rosenthal, U.; Nauck, C.; Arndt, P.; Pulst, S.; Baumann, W.; Burlakov, V. V.; Görls, H. *J. Organomet. Chem.* **1994**, *484*, 81.

(5) (a) McGinnety, J. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1038. (b) Ashworth, T. V.; Chetcuti, M. J.; Howard, J. A. K.; Stone, F. G. A.; Wisbey, S. J. *J. Chem. Soc., Dalton Trans.* **1981**, 763. (c) Farrar, D. H.; Payne, N. C. *J. Organomet. Chem.* **1981**, *220*, 239.

(6) Carriedo, G. A.; Miguel, D.; Riera, V.; Solans, X.; Font-Altaba, M.; Coll, M. *J. Organomet. Chem.* **1986**, *299*, C43.

(7) (a) Nelson, J. H.; Wheelock, K. S.; Cusachs, L. C.; Jonassen, H. B. *J. Chem. Soc., Chem. Commun.* **1969**, 1019. (b) Nelson, J. H.; Wheelock, K. S.; Cusachs, L. C.; Jonassen, H. B. *J. Am. Chem. Soc.* **1969**, *91*, 7005. (c) Wheelock, K. S.; Nelson, J. H.; Cusachs, L. C.; Jonassen, H. B. *J. Am. Chem. Soc.* **1970**, *92*, 5110. (d) Nelson, J. H.; Wheelock, K. S.; Cusachs, L. C.; Jonassen, H. B. *Inorg. Chem.* **1972**, *11*, 422. (e) Sakaki, S.; Kato, H.; Kawamura, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 195. (f) Tatsumi, K.; Fueno, T.; Nakamura, A.; Otsuka, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2170. (g) Underwood, D. J.; Nowak, M.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2837.

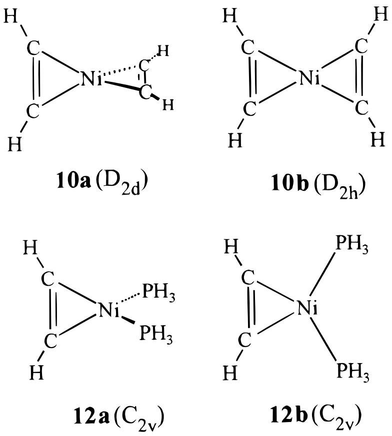
(8) See also: (a) Rösch, N.; Hoffmann, R. *Inorg. Chem.* **1974**, *13*, 2656. (b) Sakaki, S.; Hori, K.; Ohyoshi, A. *Inorg. Chem.* **1978**, *17*, 3187. (c) Albright, T. A.; Hoffmann, R.; Thibault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

(9) (a) Kitaura, K.; Sakaki, S.; Morokuma, K. *Inorg. Chem.* **1981**, *20*, 2292. (b) Ziegler, T. *Inorg. Chem.* **1985**, *24*, 1547.

(10) (a) Norman, J. G. *J. Inorg. Chem.* **1977**, *16*, 1328. (b) Åkermark, B.; Almemark, M.; Almlöf, J.; Bäckvall, J. E.; Roos, B.; Støgard, Å. *J. Am. Chem. Soc.* **1977**, *99*, 4617. (c) Ozin, G. A.; Power, W. J.; Upton, T. H.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1978**, *100*, 4750. (d) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558. (e) Sakaki, S.; Kitaura, K.; Morokuma, K.; Ohkubo, K. *Inorg. Chem.* **1983**, *22*, 104. (f) Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 1912. (g) Siegbahn, P. E. M.; Brandemark, U. B. *Theor. Chim. Acta* **1986**, *69*, 119.

(11) (a) Walther, D.; Schmidt, A.; Klettke, T.; Imhoff, W.; Görls, H. *Angew. Chem.* **1994**, *106*, 1421; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1373. (b) Walther, D.; Klettke, T.; Görls, H. *Angew. Chem.* **1995**, *107*, 2022; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1860. (c) Walther, D.; Klettke, T.; Schmidt, A. *Organometallics* **1996**, *15*, 2314.

**Scheme 3**



**10a** ($D_{2d}$) **10b** ($D_{2h}$)

**12a** ($C_{2v}$) **12b** ($C_{2v}$)

requirements for effective back-bonding into acetylene $\pi_{\|}$* orbitals in mononuclear compounds can account for the main features of molecular geometry in polynuclear compounds.

## Computational Details

The geometry optimizations have been carried out by using the DFT method[12] including the local density correlation potential by Vosko et al.[13] and Becke's three-parameter functional[14] with nonlocal correlation corrections of Lee, Yang, and Parr,[15] known in the literature by its synonym Becke3LYP. A single extended all-electron basis set was used throughout our studies. For Ni we have chosen Wachters (14s, 9p, 5d) basis set[16] augmented with a 4f polarization function ($\alpha_f = 1.29$). The contraction scheme of [9s, 5p, 3d, 1f] corresponds to a double- and triple-$\xi$ basis for the core and valence electrons, respectively. The McLean and Chandler basis set[17] was used for P, and for C and H the 6-311G basis.[18] The basis sets of P and C were augmented by a single 3d polarization function ($\alpha_p = 0.55$; $\alpha_c = 0.626$). Vibrational frequencies were obtained from analytic calculations of the Hessian matrices. Nuclear magnetic resonance (NMR) properties have been computed by using the gauge-independent atomic orbital (GIAO) method.[19] Charge reorganization in the free and coordinated ligands was calculated by using the natural population analysis (NPA) and natural bond orbital (NBO) methods.[20] In this approach the canonical MOs of the DFT wave function are transformed into localized form, i.e., into NBOs that correspond to one-center ("lone-pair") and two-center ("bond") elements of the molecular Lewis structure picture.[20] The nature and extent of charge reorganizations is characterized by comparing the occupancies of NBOs in the isolated molecular fragments with those in the complex. Binding energies were calculated at the DFT, Hartree–Fock (HF),[21] and Møller–Plesset (MP2, MP3, MP4) levels[22] as well as by using coupled-cluster theory[23] with singles and doubles (CCSD) and a noniterative estimate of triple substitutions (CCSD(T)).[24] The calculations were carried out with the Gaussian 94 package of programs.[25]

## Qualitative Picture of the Electronic Structure of Complexes 10 and 12

The basic principles of the electronic structure of complexes **10** and **12** can be easily recapitulated with help of the fragment molecular orbital approach [26] considering symmetry requirements for the possible donation and back-donation interactions. In the case of **10a** and **12b** four occupied ligand MOs have proper symmetry to mix with four empty Ni levels. Proceeding from **10a** and **12b** to **10b** and **12a**, a mismatch in symmetry arises, reducing the number of ligand-to-metal (L → M) donation interactions to three. According to the 18 valence electron (VE) rule **10a** and **12b** can be classified as 18 VE-like and **10b** and **12a** as 16 VE-like species. Nevertheless it is well-known that back-bonding in complexes **10** and **12** is by far more important than L → M bonding. In Figure 1 we show schematically the shapes of the accepting ligand levels of either conformation. For reasons of symmetry three back-bonding interactions are allowed for **10a** (e, $b_1$) and only two for **10b** ($b_{3g}$, $b_{1g}$).

Thus with respect to **10a**, **10b** is characterized by diminished L → M bonding as well as diminished M → L back-bonding. The latter interaction concerns the acetylene $\pi_{\|}$* MO, while acceptor properties of the $\pi_{\perp}$* MO should be of comparable magnitude in both conformations. Due to the $\delta$ character of the out-of-plane back-bonding, its contribution to the whole bonding is by far less important. For complexes **12** the symmetry

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[12] (a) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133. (b) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989. (c) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jeckson, K.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671. (d) Laird, B. B., Ross, R. B., Ziegler, T., Eds. *Chemical Applications of Density Functional Theory*; ACS Symp. Ser. 629; American Chemical Society: Washington, DC, 1996.

[13] Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

[14] Becke, A. D. *J. Chem. Phys.* **1992**, *96*, 2155; **1993**, *98*, 5648.

[15] (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

[16] Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

[17] McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

[18] Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

[19] (a) London, F. J. *J. Phys. Radium* **1937**, *8*, 397. (b) McWeeny, R. *Phys. Rev.* **1962**, *126*, 1028. (c) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. (d) Dodds, J. L.; McWeeny, R.; Sadlej, A. J. *Mol. Phys.* **1980**, *41*, 1419. (e) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

[20] (a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066. (c) Read, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (d) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (e) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 41.

[21] Roothaan, C. C. *J. Rev. Mod. Phys.* **1951**, *23*, 69.

[22] Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

[23] (a) Cizek, J. *J. Chem. Phys.* **1966**, *45*, 4256; *Adv. Chem. Phys.* **1969**, *14*, 35. (b) Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 516.

[24] (a) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *14*, 545. (b) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. (c) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968. (d) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 7041. (e) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1988**, *89*, 7382. (f) Scuseria, G. E.; Schaefer, H. F., III. *J. Chem. Phys.* **1989**, *90*, 3700.

[25] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94 Revision D.2*; Gaussian, Inc.: Pittsburgh, PA, 1995.

[26] Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

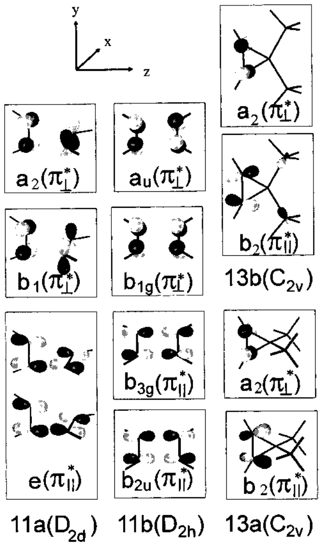

**Figure 1.** Symmetry and shapes of the accepting ligand levels $(C_2H_2)_2$−**11** and $[C_2H_2-(PH_3)_2]$−**13**.

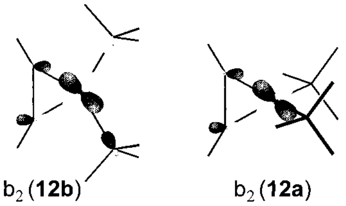

**Figure 2.** Back-bonding interactions in complexes **12b** and **12a**.

of the acetylene accepting levels is preserved on transformation of planar **12b** into twisted **12a**. Consequently M → L back-bonding should be of the same character in both conformations. Thus for **12** symmetry requirements suggest equal M → L back-donation in both **12a** and **12b** with reduced L → M donative interaction in **12a**. However, transformation from planar **12b** to twisted **12a** leads to a change in symmetry ($b_2 \rightarrow b_1$) of the occupied phosphorus lone-pair combination. In **12b** this $b_2$ combination can transfer electron density through the $b_2$ ($d_{yz}$) Ni level into the acetylene $\pi_{||}$* MO. This interaction is not possible in **12a** due to symmetry constraints (Figure 2).

Again, acceptor properties of the acetylene $\pi_\perp$* MO should be low in both conformations. In summary, upon going from the existing **10a** and **12b** to the hypothetical molecules **10b** and **12a**, diminished L → M donation as well as diminished M → L back-donation into the acetylene in-plane $\pi_{||}$* MO should be observed due to symmetry constraints.

NBO population analysis carried out for the DFT wave function of the optimized conformers confirms the qualitative picture concerning back-bonding interactions. For either conformation the population of acetylene $\pi_\perp$* NBO is low (<0.054*e*), but large population by 0.471*e* (**10a**), 0.245*e* (**10b**), 0.407*e* (**12a**), and 0.605*e* (**12b**) is found for the in-plane $\pi_{||}$* NBO with a sufficiently large difference between the two conformers to account for the rotational preference of **10a** and **12b** over **10b** and **12a**. For complexes **12** donor−acceptor abilities of Ni are of comparable magnitude for both conformations. The calculated natural charge on Ni amounts to +0.613 for **12b** and +0.619 for **12a**. The additional amount of electron density transferred to the acetylene $\pi_{||}$* NBO in **12b** correlates well with electron density depopulation on the phosphorus lone-pair NBO (1.854*e* (**12a**), 1.754*e* (**12b**)). For L → M donation interaction the NBO population analysis predicts that occupation of Ni 4p levels in both types of complexes **10** and **12** remains negligible (<0.005*e*) even in those cases where it is symmetry permitted. L → M donative interactions are found to be effective only in the case of Ni 4s (0.336*e* (**10a**), 0.298*e* (**10b**), 0362*e* (**12a**), and 0.378*e* (**12b**)). If in the electron-counting scheme only those ligand electrons effectively donated to the metal were taken into consideration, a 12 VE configuration would result for all conformations under consideration.

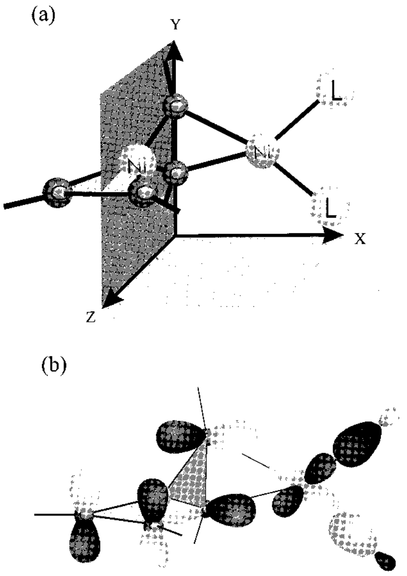

**Figure 3.** (a) Our coordinate system for bonding of **10a** with the $NiL_2$ fragment to give **8**. (b) Back-bonding interaction from Ni $d_{xy}$ and lone-pair MOs of $\sigma$-donor ligands into the $a_2$ MO of **10a** in complexes of type **8**.

## Bonding and Molecular Geometry of Polynuclear Ni(0) Complexes

A preliminary understanding of the electronic structure and molecular geometry of di- and polynuclear complexes of alkynes with Ni(0) can be easily derived from the preceding analysis of the mononuclear model compounds of type **10** and **12**. The following considerations focus on the back-bonding into alkyne in-plane $\pi_{||}$* MOs as the main source of rotational preference in mononuclear compounds. Figure 3a depicts a dinuclear compound of type **8** build up from $(C_2H_2)_2Ni$−**10a** and the metal fragment $NiL_2$ (L = $\sigma$-donor ligand). The bridging alkyne is orientated alongside the *Y*-axis of our coordinate system.

In fragment **10a** the $\pi_z$* MO of the bridging acetylene is part of the in-plane e ligand combination of **11a** (see Figure 1) and is strongly populated due to back-bonding interaction within the **10a** moiety. The $\pi_x$* MO of the bridging acetylene is involved in the out-of-plane $b_1$ and $a_2$ combinations which are of little and of no extent in the case of $a_2$ populated by back-bonding within **10a**. Thus $\pi_x$* of the bridging acetylene lends itself more easily to effective back-bonding interactions with the second metal fragment than $\pi_z$* and must be considered

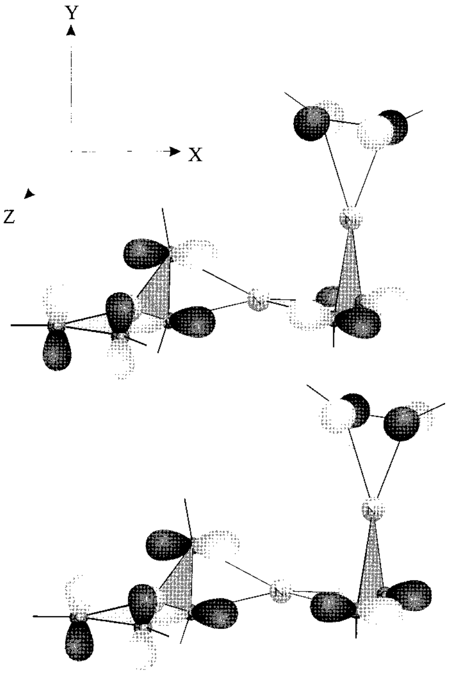

**Figure 4.** In-phase and out-of-phase combinations of $a_2$ MOs of two isolated molecules **10a** in complexes of type **9**.

the preferred target for further coordination. In order for back-bonding into $\pi_x$* of the bridging acetylene to be in-plane, the $NiL_2$ fragment will have to come to lie in the *XY*-plane. In this situation each $\pi$* MO of the bridging acetylene is in-plane and strongly bonding with respect to one moiety and out-of-plane and weakly bonding with respect to the other moiety. The relative orientation of the individual molecular fragments with respect to the bridging alkyne follows the same rules as for the mononuclear complexes **10** and **12**. These basic geometrical requirements are discernible in both the trinuclear complexes of type **9** and **6** and the binuclear complexes of type **8** and **3**−**5**.

Figure 3b schematically depicts the ligand $a_2$ combination of **10a** that is inactive with respect to back-bonding within the bis(alkyne)Ni moiety in connection with the out-of-phase combination of the lone-pairs of $\sigma$-donor ligands. The latter is involved in back-bonding interactions of the Ni $d_{xy}$ level similar to those of the $b_2$ MO in the case of the mononuclear complex **12b** (Figures 3 and 2). Similarly, the geometrical requirements of effective back-bonding can account for the main features of molecular structure in the trinuclear complexes of type **9**. In Figure 4, two $Ni(C_2H_2)_2$ molecules **10a** are arranged in such a way as to provide the preferred tetrahedral conformation for the central Ni atom. The two bridging alkynes are orientated alongside the *Y*- and *Z*-axis.

The "ligand combination" for the central Ni atom is formed by in-phase and out-of-phase combinations of the MOs of two isolated molecules **10a**. Figure 4 displays the two possible combinations of the $a_2$ MOs of the isolated molecules **10a**. The four lobes adjacent to the central Ni atom can be easily correlated with the degenerated e levels of acetylene dimer **11a** from Figure 1. Thus in complexes **9** the combinations of the inactive $a_2$ out-of-plane acceptors of the terminal units provide the in-plane main acceptor levels to the central unit. Formation of polynuclear complexes with general formula $Ni_n(RC{\equiv}CR)_{n+1}$ should be possible by subsequent coupling of terminal alkynes with Ni(0) species.

**Table 1. Calculated Occupancies and Net Charge for Terminal and Bridging Acetylenes in 14 and 23**

| | terminal $C_2H_2$ | | | bridging $C_2H_2$ | |
|---|---|---|---|---|---|
| NBO | **10a** | **14** | **23** | **14** | **23** |
| $\pi_\perp$ | 1.949 | 1.952 | 1.955 | 1.861 | 1.869 |
| $\pi_\parallel$ | 1.840 | 1.843 | 1.845 | 1.773 | 1.768 |
| $\pi_\perp$* | 0.036 | 0.037 | 0.036 | 0.372 | 0.331 |
| $\pi_\parallel$* | 0.471 | 0.460 | 0.452 | 0.625 | 0.631 |
| $q(C_2H_2)$ | −0.389 | −0.382 | −0.379 | −0.755 | −0.728 |

This qualitative picture of the bonding in polynuclear compounds is directly supported by NBO population analysis carried out for the model compounds **14** and **23**. The calculated natural charge of Ni atoms in **14** (+0.760) does not differ much from that in **10a** (+0.779). The natural charge of the central Ni atom of **23** is slightly less positive (+0.708), and that for terminal Ni atoms amounts to +0.752. The electron density distribution in the $\pi$ orbitals of terminal acetylenes is almost the same as in the mononuclear complex **10a** and corresponds to strong in-plane and weak out-of-plane donor−acceptor interactions (Table 1).

In the case of bridging acetylenes strong out-of-plane shifts of electron density in addition to strong in-plane reorganization are discernible. As a result of these donor−acceptor interactions, the calculated natural net charge on bridging acetylene is almost 2 times greater than for the terminal ones (Table 1). These results clearly show that the bonding of bridging alkynes is achieved due to donor−acceptor activities of both alkyne $\pi$ systems, while the bonding of terminal alkynes is similar to that of alkenes.[8,10g]

## Molecular Geometries, Vibrational Frequencies, and NMR Properties

Fully optimized geometrical parameters of complexes **10**, **12**, and **14** are shown in Figure 5, and those of the free ligands **15**, **15a**, and **16** are displayed in Figure 6.

To our knowledge no X-ray data of the alkyne **15a** are available. For **15a** the calculations predict linear conformation of the C−C≡C−C moiety and suggest that $CEt_2OH$ substituents have no considerable effect on the C≡C bond distance (Figure 6). The coordinated alkynes are no longer linear but adopt a cis bent structure. In the case of **12b** the optimized HC≡C bond angle of 147.5° reproduce the experimental value of 148° found for $(P(Ph)_3)_2Ni(C_2H_2)$.[4g] The reasons for the deviation from linearity of coordinated alkynes were discussed in detail in the literature.[27] The experimental bond distances and angles of Ni−alkyne complexes depend on the nature of alkyne substituents and of the $\sigma$-donor ligands.[4,11] Nevertheless all optimized parameters of the model complexes **10a** and **12b** are within the ranges of known experimental values of the parent complexes **7** and **2** (M = Ni) (Table 2).

In the case of the mononuclear compounds the optimized C≡C bond distance of complexed acetylene is elongated with respect to the free ligand by 0.063 Å (**10a**), 0.035 Å (**10b**), 0.048 Å (**12a**), and 0.075 Å (**12b**).

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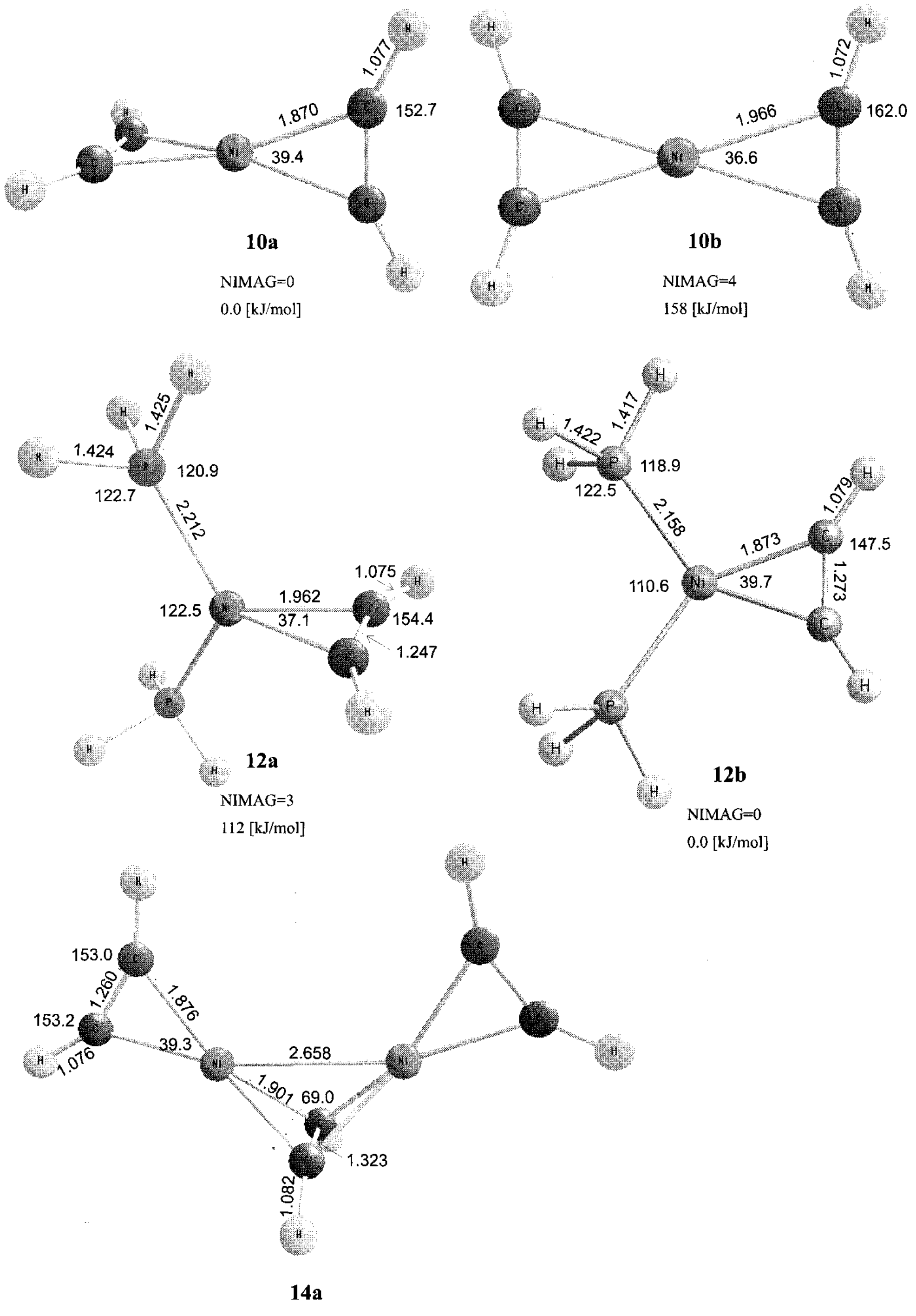
(27) (a) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858. (b) Hoffman, D. M.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* **1982**, 1471.



**10a**
NIMAG=0
0.0 [kJ/mol]

**10b**
NIMAG=4
158 [kJ/mol]

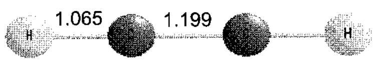
**12a**
NIMAG=3
112 [kJ/mol]

**12b**
NIMAG=0
0.0 [kJ/mol]

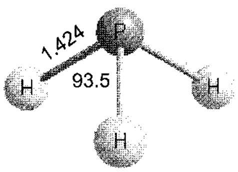
**14a**
NIMAG=0

**Figure 5.** Optimized geometrical parameters and relative energies of **10a**, **10b**, **12a**, **12b**, and **14** (Becke3LYP results). Bond distances are given in angstroms, bond angles in degrees.

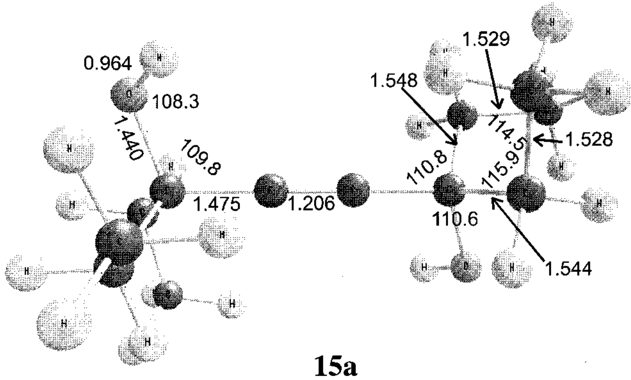
The calculations yield an elongation of the Ni−C distance on going from preferred structures, the quasi-tetrahedral **10a** and planar **12b**, to hypothetical **10b** (planar) and **12a** (twisted) by 0.096 and 0.089 Å, respectively. The predicted increase in energy is 158 kJ/mol for **10a** → **10b** and 112 kJ/mol for **12b** → **12a**. The vibrational analysis carried out for **10b** and **12a** indicates that both conformers correspond neither to an energy minimum nor to a transition state on the potential energy surface. **10b** has four ($a_u$ (606i), $b_{2u}$ (391i), $b_{3u}$ (178i), $b_{2u}$ (67i) $cm^{-1}$) and **12a** three ($a_2$ (289i), $b_1$ (70i), $a_2$ (34i) $cm^{-1}$) imaginary modes. **10a** and **12b** have all real frequencies and represent the global minima. The optimized geometrical parameters of terminal acetylenes in the binuclear model complex **14** are almost the same as those in **10a** (Figure 5). With respect to terminal acetylenes the C−C bond length of bridging acetylene is by 0.063 Å longer and deviates only slightly from a normal C=C bond distance (1.34 Å). The long Ni−Ni distance of 2.658 Å suggests that bonding Ni−Ni interactions are not present in **14**. The lengthening of the C≡C bond of coordinated alkynes is usually discussed as a result of electron density back-donation from the metal to alkyne $\pi^*$ MOs. Notably, alkyne C≡C stretch frequencies and NMR $^{13}C\equiv$ chemical shifts are used as a very sensitive measure for electron density



**15**



**16**



**15a**

**Figure 6.** Optimized geometries of acetylene−**15**, alkyne−**15a**, and $PH_3$−**16** (Becke3LYP results). Bond distances are given in angstroms; bond angles in degrees.

**Table 2. Comparison of Data Calculated for 10a and 12b with Experimental Results of Complexes 7 and 2 (M = Ni)**[a]

| | calc **10a** | expt (ref 11) **7** | calc **12b** | expt (ref 4) **2** (M = Ni) |
|---|---|---|---|---|
| $d$(C≡C) | 1.261 | 1.259−1.278 | 1.273 | 1.239−1.282 |
| $d$(Ni−C) | 1.870 | 1.869−1.888 | 1.873 | 1.848−1.927 |
| ∠CNiC | 39.4 | 39.0−39.8 | 39.7 | 38.1−42.1 |
| ∠R/HC≡C | 152.7 | 152.5−156.0 | 147.5 | 134.9−149.4 |
| $d$(Ni−P) | | | 2.158 | 2.152−2.211 |
| ∠PNiP | | | 110.6 | 102.7−117.8 |
| $\Delta\nu_{C\equiv C}$ | 286 | 325−347 | 339 | 344−510 |
| $\Delta\delta(^{13}C\equiv)$ | 60.7 | | 56 | 35.5−55.1 |

[a] Distances are given in angstroms, bond angles in degrees, $\Delta\nu_{C\equiv C}$ in $cm^{-1}$, and $\Delta\delta(^{13}C\equiv)$ in ppm.

reorganization upon alkyne coordination. With respect to free alkynes the C≡C stretch frequency of complexes **7** and **2** (M = Ni) is shifted 325−510 $cm^{-1}$ toward lower wavenumbers, depending on the nature of the coordinated ligands.[4,11,28] With respect to free acetylene the calculated shift of the C≡C stretch frequency ($\Delta\nu_{C\equiv C}$) amounts to 286 $cm^{-1}$ for **10a** and 339 $cm^{-1}$ for **12b**. The calculated $\Delta\nu_{C\equiv C}$ of **12b** agrees very well with the experimental value of 344 $cm^{-1}$ obtained for $(PPh_3)_2Ni(C_2H_2)$.[4g] In the case of the binuclear complex **14**, $\Delta\nu_{C\equiv C}$ amounts to 552 and 294 $cm^{-1}$ for bridging and terminal acetylene, respectively. These values suggest that a linear relationship may exist between $\Delta\nu_{C\equiv C}$ and the strength of electron density back-donation expressed by occupation numbers of acetylene $\pi^*$ orbitals, OCC ($\pi^*$). A rough estimate based on calculated data of complexes **10**, **12**, and **14** leads to eq 1.[29]

$$\Delta\nu_{C\equiv C} \times 10^{-3} \approx 0.558\mathrm{OCC}(\pi^*) \qquad (1)$$

A linear correlation is also found for the optimized C≡C bond distance and the strength of electron density back-donation (eq 2).

$$d_{C\equiv C} \approx 1.718\mathrm{OCC}(\pi^*) + 1.2 \qquad (2)$$

It is interesting to note that similar conclusions were found for carbonyl complexes $M(CO)_6$ and $M(CO)_5L$.[30]

Computations of NMR properties can be now routinely performed at HF, post-HF,[31] and DFT levels of theory.[32] Nevertheless much less is known about calculated NMR data in the case of transition metal compounds, for which one may expect that effects of electron correlation can affect the results of NMR calculations significantly. Recent investigations of Ziegler et al.[33] and Malkin et al.[34] demonstrated that calculations of NMR properties of transition metal compounds are feasible with DFT methods. In Table 3 we present calculated $^1H$ and $^{13}C$ chemical shifts with respect to tetramethylsilane (TMS) in optimized geometry for free acetylene **15** and alkyne **15a** as well as for **10a**, **7a**, and **12b**.

These calculations were carried out by using the GIAO method.[19,33] The theoretical NMR results from Table 3 agree well with available experimental data. Calculated $\Delta\delta(^{13}C\equiv)$ for **12b** differs by 5.1 ppm from the

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[28] Klettke, T. Dissertation, University of Jena, 1997.

[29] Other alkyne complexes also follow this relation: Koch, J. Dissertation, University of Heidelberg, 1997.

[30] Ehlers, A. W.; Dapprich, S.; Vyboishchikov, S. F.; Frenking, G. *Organometallics* **1996**, *15*, 105.

[31] (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. (c) Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR−Basic Principles and Progress*; Springer-Verlag: Berlin, 1990; Vol. 23, p 165.

[32] (a) Bieger, W.; Seifert, G.; Eschrig, H.; Grossmann, G. *Chem. Phys. Lett.* **1985**, *115*, 275. (b) Freier, D. A.; Fenske, R. F.; Xiao-Zeng, Y. *J. Chem. Phys.* **1985**, *83*, 3526. (c) Malkin, V. G.; Zhidomirov, G. M. *Zh. Strut. Khim.* **1988**, *29*, 32. (d) Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *Chem. Phys. Lett.* **1993**, *204*, 80; **1993**, *204*, 87 (e) Salahub, D. R.; Fournier, R.; Mlynarski, P.; Papai, I.; St.-Amant, A.; Ushio, J. In *Density Functional Methods in Chemistry*; Labanowski, J., Andzelm, J., Eds.; Springer: New York, 1991; p 77. (f) Malkin, V. G.; Malkina, O. L.; Erikson, L. A.; Salahub, D. R. In *Modern Density Functional Theory: A Tool for Chemistry*; Vol 2 of Theoretical and Computational Chemistry; Politzer, P., Seminario, J. M., Eds.; Elsevier: Amsterdam, 1995.

[33] (a) Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.* **1995**, *99*, 606. (b) Schreckenbach, G.; Dickson, R. M.; Ruiz-Morales, Y.; Ziegler, T. In ref 12d, p 328.

[34] (a) Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898. (b) Kaupp, M.; Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 1851.

**Table 3. NMR $^{13}$C and $^{1}$H Chemical Shifts (ppm) Relative to TMS**

| | 15 | | 15a | | 7a | | 10a | 12b | |
|---|---|---|---|---|---|---|---|---|---|
| | calc | expt[a] | calc | expt[b] | calc | expt[b] | calc | calc | expt[c] |
| $^{13}$**C**≡ | 71.2 | 71.9 | 93.0 | 86.9 | 142.0 | 133.3 | 131.9 | 127.2 | 122.8 |
| $^{13}$**C**−C≡ | | | 76.9 | 72.1 | 67.9 | 74.3 | | | |
| $CH_3$−$^{13}$**C**$H_2$−C−C≡ | | | 37.7 | | 36.3 | 35.4 | | | |
| $^{13}$**C**$H_3$−$CH_2$−C−C≡ | | | 10.1 | | 5.1 | 9.1 | | | |
| $^{1}$**H**−C≡ | 1.3 | 2.4 | | | | | 7.2 | 7.2 | 6.4 |
| $^{1}$**H**$^{3}$−$CH_2$−C−C≡ | | | 1.0 | | 1.5 | 1.0 | | | |
| $CH_3$−$^{1}$**H**$_2$C−C−C≡ | | | 1.8 | | 1.8 | 1.7 | | | |

[a] Ref 35. [b] Refs 11, 28. [c] Data of $(PPh_3)_2Ni(C_2H_2)$ from ref 4g.

**Table 4. Binding Energies (kJ/mol) of Acetylene, Ethylene,and Carbon Monoxide for Mononuclear Ni(0) Complexes 10a, 12b, and 17−22 Calculated at Different Levels of Theory**

| compd | Dissociation pattern | DFT | CCSD(T) | CCSD | MP4(SDQ) | MP4(DQ) | MP3 | MP2 | HF |
|---|---|---|---|---|---|---|---|---|---|
| **10a** | $Ni(C_2H_2)_2 \rightarrow Ni(C_2H_2) + C_2H_2$ | 288 | 280 | 242 | 546 | 528 | 124 | 566 | 90 |
| **17** | $Ni(C_2H_4)_2 \rightarrow Ni(C_2H_4) + C_2H_4$ | 227 | 219 | 179 | 518 | 463 | 58 | 490 | 55 |
| **18** | $Ni(C_2H_2)(C_2H_4) \rightarrow Ni(C_2H_4) + C_2H_2$ | 259 | 251 | 212 | 498 | 453 | 98 | 480 | 83 |
| **18** | $Ni(C_2H_2)(C_2H_4) \rightarrow Ni(C_2H_4) + C_2H_4$ | 253 | 246 | 210 | 512 | 470 | 99 | 513 | 66 |
| **20** | $Ni(CO)_4 \rightarrow Ni(CO)_3 + CO$ | 86 | 104 | 70 | 676 | 488 | −162 | 222 | −14 |
| **21** | $Ni(CO)_3 \rightarrow Ni(CO)_2 + CO$ | 151 | 157 | 139 | 412 | 342 | 6 | 248 | 60 |
| **22** | $Ni(CO)_2 \rightarrow Ni(CO) + CO$ | 222 | 188 | 153 | 517 | 418 | 41 | 394 | 89 |
| **12b** | $Ni(PH_3)_2(C_2H_2) \rightarrow Ni(PH_3)_2 + C_2H_2$ | 221 | 262 | 253 | 163 | 146 | 240 | 160 | 192 |
| **19** | $Ni(PH_3)_2(C_2H_4) \rightarrow Ni(PH_3)_2 + C_2H_4$ | 198 | 237 | 227 | 206 | 188 | 202 | 209 | 155 |

**Table 5. Comparison of Experimental CO Bond Energies with Available Theoretical Data for Nickel Carbonyls 20−22 (All Values Are Given in kJ/mol)**

| method | ref | $Ni(CO)_4$−**20** | $Ni(CO)_3$−**21** | $Ni(CO)_2$−**22** |
|---|---|---|---|---|
| expt | 36a | 105 ± 8 | 54 ± 42 | 226 ± 63 |
| | 36b | 90 ± 2 | | |
| | 36c | 92 ± 4 | 118 ± 10 | 197 ± 24 |
| MCPF | 37a,b | 100 | 150 | 121 |
| | 37g | 88 | 139 | 129 |
| PCI-80 | 37g | 110 | 164 | 138 |
| CASPT2 | 37h | 103 | 145 | 178 |
| CCSD(T) | 37c | 125 | 145 | 178 |
| | 37d | 99 | | |
| | 30 | 93 | | |
| | this work | 104 | 157 | 188 |
| DFT | 37e | 106 | | |
| | 37f | 125−188 | | |
| | 37g | 86 | 121 | 170 |
| | this work | 86 | 151 | 222 |

experimental value of $(PPh_3)_2Ni(C_2H_2)$,[4g] and those of **7a** differ by 2.6 ppm.[11,28] To finish this section we notice that experimental and computed structural and spectroscopic data consistently suggest a weakening of the triple-bond of coordinated alkynes, which according to NBO population analysis mainly stems from metal−ligand back-donation into the alkyne $\pi_{||}$* MO and to a lesser extent from a transfer of charge from the alkyne occupied $\pi$ orbital into the Ni 4s level.

## Binding Energies of Ligands in Mononuclear Ni(0) Compounds

The calculated binding energies (BEs) of acetylene are collected in Table 4. In view of our interpretation of the bonding of terminal acetylenes as ethylene-like, we have also calculated the BEs for the corresponding ethylene complexes **17**−**19**. To obtain more insight in the postulated isolobal relationship of acetylene with two two-electron ligands,[7g] we present in Table 5 the BEs of carbon monoxide calculated for the experimentally[36] and theoretically[37] well characterized nickel carbonyls **20**−**22**. The small size and high symmetry of the investigated mononuclear compounds allow for a comparison of computed DFT BEs with values obtained at other theoretical levels. The BEs at the HF, MP2-MP4, CCSD, and CCSD(T) levels were calculated for DFT fully optimized molecular structures. A comparison of BEs from different levels of theory should be helpful for an understanding of the importance of electron correlation as well as for an assessment of the reliability of the particular values. Furthermore, a comparison of DFT and CCSD(T) BEs will be helpful for our discussion concerning polynuclear compounds where application of post-HF electron correlated techniques is computationally prohibitive.

The data from Table 4 demonstrate that the contribution of electron correlation to BEs shows marked differences for various types of Ni(0) compounds. While correlation plays only a minor role for complexes **12b** and **19**, it becomes dominant in the bonding of alkyne and alkene complexes **10a**, **17**, and **18** as well as for nickel carbonyls **20**−**22**. In the case of **12b** and **19** the HF result accounts for 73% (**12b**) and 65% (**19**) of the BE calculated at the CCSD(T) level. This situation is reversed for complexes **10a**, **17**, and **18**, where about 70% of the CCSD(T) BE is due to correlation. For $Ni(CO)_4$−**20** the fourth carbonyl ligand is unbound at the HF level and chemical bonding must be entirely attributed to electron correlation. Similar arguments were presented by Davidson et al. for $Cr(CO)_6$.[38] The authors found that the mean dissociation energy of CO in $Cr(CO)_6$ is approximately equal to the correlation energy.[38] As must be expected,

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(35) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH Verlagsgesellschaft: Weinheim, 1993.

(36) (a) Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 5026. (b) Day, J. P.; Basolo, B.; Pearson, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 6927. (c) Sunderlin, L. S.; Wang, D.; Squires, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 2788.

(37) (a) Blomberg, M. R. A.; Brandemark, U. B.; Siegbahn, P. E. M.; Wennerberg, J.; Bauschlicher, C. W., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 6650. (b) Bauschlicher, C. W., Jr.; Langhoff, S. R. *Chem. Phys.* **1989**, *129*, 431. (c) Blomberg, M. R. A.; Siegbahn, P. E. M.; Lee, T. J.; Rendell, A. P.; Rice, J. E. *J. Chem. Phys.* **1991**, *95*, 5898. (d) Ehlers, A. W.; Frenking, G.; *Organometallics* **1995**, *14*, 423. (e) Ziegler, T.; Tschinke, V.; Ursenbach, Ch. *J. Am. Chem. Soc.* **1987**, *109*, 4825. (f) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486. (g) Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. *J. Chem. Phys.* **1996**, *104*, 9546. (h) Persson, B. J.; Roos, B. O.; Pierloot, K. J. *Chem. Phys.* **1994**, *101*, 6810.

**Table 6. Energy (kJ/mol) of the Association Reactions of the Third Ligand L′ to $NiL_2$ Species Calculated with the Becke3LYP Method**

| | L′ | | |
|---|---|---|---|
| $NiL_2$ | CO | $PH_3$ | $C_2H_2$ |
| $Ni(CO)_2$ | −151 | −94 | −180 |
| $Ni(PH_3)_2$ | −199 | −109 | −221 |
| $Ni(C_2H_2)_2$ | −98 | −32 | −32 |

the performance of Møller−Plesset perturbation theory methods varies considerably with the extent of electron correlation. For complexes **10a**, **17**, **18**, and **20**−**22** nonrealistic BEs are calculated at the MP2−MP4 levels (Table 4). This is not surprising because all perturbational methods are based on the assumption that perturbation, i.e., in this case electron correlation, should be small, which does not hold for these compounds. A number of conclusions concerning bonding and stability of Ni(0)−alkyne complexes can be drawn from the data in Table 4. The BE of acetylene in **10a** and **12b** is somewhat greater than those of ethylene in **17** and **19**. This can be attributed to the small bonding contribution of acetylene's second $\pi$ system in **10a** and **12b**, which is not possible for **17** and **19**. X-ray investigations on complexes **7** showed that these compounds adopt a supramolecular structure.[11,28] It was postulated that hydrogen bonds between OH groups of neighboring $(RC{\equiv}CR)_2Ni$ molecules are responsible for the stability of bis(alkyne) Ni compounds in the solid state. A question arises whether hydrogen bonds are prerequisites for the thermodynamic stability of these compounds. From the values given in Table 4 we notice that energy gain due to the bonding of acetylene with the $Ni(C_2H_2)$ fragment to give **10a** (280 kJ/mol) is remarkable and even greater than for the coordination of two CO molecules to $Ni(CO)_2$ to give $Ni(CO)_4$ (261−270 kJ/mol). This finding that one acetylene ligand in some chemical environments can stabilize the Ni(0) moiety to roughly about the same extent as two CO ligands seems to corroborate Hoffmann's isolobal analogy between one acetylene and two carbonyl ligands.[7g] On the other hand an exchange of four CO ligands of **20** by two acetylenes is calculated to be endothermic by 153 and 184 kJ/mol at the CCSD(T) and Becke3LYP levels, respectively.

$$Ni(CO)_4 + 2C_2H_2 + \Delta E \rightarrow Ni(C_2H_2)_2 + 4CO \quad (3)$$

We think that the endothermicity $\Delta E$ from reaction 3 can be inherently connected with a higher degree of saturation of the $Ni(CO)_4$ complex respective to $Ni(C_2H_2)_2$.

Undoubtedly the remarkable BE of acetylene in **10a** is the main reason for the *thermodynamic* stability of this compound. However, *kinetic* stability of the formally two-coordinated **10a** should be strongly associated with its degree of unsaturation. As a natural measure for an unsaturated character of transition metal species, we choose the exothermicity of the association reactions with additional donor ligands. In Table 6 we compare the calculated with the Becke3LYP method energy of the association reaction of the third ligand L′ to $NiL_2$ species (L, L′ = CO, $PH_3$, $C_2H_2$) (eq 4)

$$NiL_2 + L' \rightarrow NiL_2L' \quad (4)$$

As can be seen from Table 6 the exothermicities of the association reactions to $Ni(CO)_2$, a highly reactive intermediate observed in the decomposition of $Ni(CO)_4$ by matrix isolation technique as well as to the model molecule $Ni(PH_3)_2$, are significantly greater than in the case of $Ni(C_2H_2)_2$−**10a**. At this point we conclude that the degree of saturation of **10a** is greater than for the species conventionally characterized as 14 VE $NiL_2$ (L = CO, $PH_3$) but lower than for the 18 VE $Ni(CO)_4$ complex. The calculation with the Becke3LYP method energy of the association reaction of the fourth ligand L to the $NiL_3$ species (eq 5) amounts to −86 kJ/mol for L = CO; −76 kJ/mol for L = $PF_3$; −58 kJ/mol for L = $PMe_3$; −55 kJ/mol for L = $PH_3$; and +63 kJ/mol for L = $C_2H_2$.

$$NiL_3 + L \rightarrow NiL_4 \quad (5)$$

The fourth acetylene ligand is unbound in $Ni(C_2H_2)_4$. The calculated energies of the reactions from eqs 3−5 suggest that the degree of saturation of **10a** is best described as similar to that of 16 VE $NiL_3$ (L = $\sigma$-donor ligand) species. Thus assuming a kinetic stability, similar to $NiL_3$ species and given their marked thermodynamic stability we believe that bis(alkyne)Ni(0) complexes of the type of **10a** without OH groups in alkyne substituents can be present as intermediates in organometallic reactions. However hydrogen bonds might be crucial for their crystallization.

## Binding Energies of Bridging and Terminal Acetylenes in 14

The good agreement of DFT BEs with CCSD(T) values for complexes **10a**, **17**, and **18** (Table 4) shows that the Becke3LYP method accounts correctly for correlation effects in this class of compounds, and we felt encouraged to apply this method for the study of BEs in the case of acetylene nickel polynuclear compounds. From the finding that acetylene in a bridging position provides for both donation and back-donation interactions nearly twice as much bonding capacity as in a terminal position (Table 1), one might expect a bridging acetylene to yield twice as much binding energy as a terminal one. The calculated bond energy of terminal acetylene in **14** amounts to 272 kJ/mol, and that of bridging acetylene, 567 kJ/mol (Scheme 4a, c). We keep in mind that Becke3LYP BE of "terminal" acetylene in **10a** amounts to 288 kJ/mol. The energy for a process where only one $\pi$ system of bridging acetylene is broken amounts to 279 kJ/mol (Scheme 4b).

In **14** the bonding capacity of the bridging acetylene's "second" $\pi$ system is 9 kJ/mol lower than that of its "first" $\pi$ system in **10a**. Consequently, the condensation reaction from eq 6 is 9 kJ/mol endothermic.

$$2Ni(C_2H_2)_2 \Leftrightarrow Ni_2(C_2H_2)_3 + C_2H_2 \quad (6)$$

The endothermicity of reaction 6 suggests that some additional bonding contributions have to be operative to facilitate the formation of polynuclear, homoleptic

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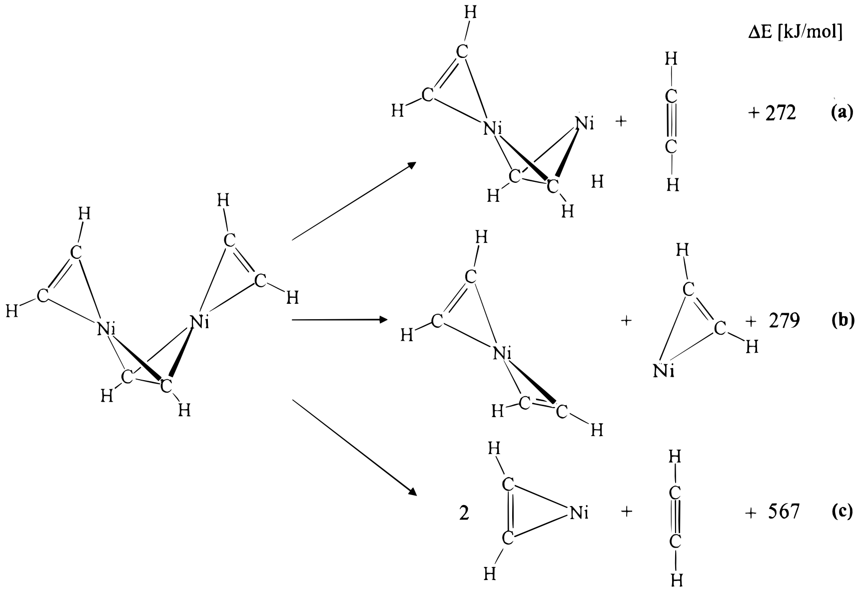
(38) (a) Davidson, E. R.; Kunze, K. L.; Machado, F. B. C.; Chkravotry, S. J. *Acc. Chem. Res.* **1993**, *26*, 628 (b) Kunze, K. L.; Davidson, E. R. *J. Phys. Chem.* **1992**, *96*, 2129.

**Scheme 4**



alkyne−nickel$^{(0)}$ compounds. A detailed discussion will be the subject of a subsequent paper.[39]

## Summary

Qualitative considerations of the number of symmetry-permitted ligand−metal (L → M) donation interactions allow the classification of the complexes of type **10a** and **12b** as 18 VE-like species and those of type **10b** and **12a** as 16 VE ones. DFT NBO population analysis indicates that within symmetry-permitted L → M donative interactions only the Ni 4s AO is effectively populated and suggests a 12 VE configuration for each conformation. The rotational preference of acetylene originates from M → L back-donation into the acetylene(s) in-plane $\pi_{\|}$* MO(s), which in **10b** and **12a** are weaker than in **10a** and **12b** due to symmetry requirements. Back-bonding interactions into alkyne in-plane $\pi_{\|}$* MO account also for the main features of molecular geometry of polynuclear Ni(0) compounds. The bonding of bridging alkynes is achieved due to donor−acceptor activities of both alkyne $\pi$ systems, and the bonding of terminal alkynes is alkene-like. The theoretically predicted structural and spectroscopic properties of the investigated complexes are in good agreement with experimental data. From the BEs calculated at different levels of theory it follows that the contribution of electron correlation shows marked differences for various types of Ni(0) compounds. Electron correlation plays a minor role for $L_2Ni$ (alkyne/alkene) compounds (L = $\sigma$-donor ligand) but becomes dominant for (alkyne/alkene)$_2$Ni and nickel carbonyls. The Becke3LYP method accounts correctly for correlation effects in (alkyne/alkene)$_2$Ni compounds. For complexes $(PH_3)_2Ni(C_2H_2)$/$(C_2H_4)$, $Ni(CO)_4$, and $Ni(CO)_2$ Becke3LYP calculated BEs differ by up to 41 kJ/mol from CCSD(T) values. In some other calculations carried out in our laboratory on some Ni(0) complexes containing the “theoretically difficult” P atoms we found that on going to extended basis sets with polarization functions of high angular quantum number Becke3LYP computes thermochemical data that are in good agreement with the experiment.[29]

The calculated BEs seem to corroborate Hoffmann’s isolobal analogy between one acetylene and two $\sigma$-donor ligands and from a thermodynamic point of view characterize $(C_2H_2)_2Ni$ as a stable compound. The calculated energies of the association reactions $NiL_n + L \rightarrow NiL_{n+1}$ ($n = 2, 3$; L = two-electron donors, $C_2H_2$) suggest that the degree of saturation of the formally two-coordinated $(C_2H_2)_2Ni$ complex is similar or even greater than that of the conventionally classified as 16 VE species, $NiL_3$ compounds (L = $\sigma$ donors). Each of the two $\pi$ systems of a bridging acetylene contribute to the bonding approximately the same amount of energy as one $\pi$ system of a terminal acetylene.

**Acknowledgment.** This paper is dedicated to Professor Zvonimir B. Maksic on the occasion of his 60th birthday. Our work was supported by BMBF (Katalyse), Deutsche Forschungsgemeinschaft, and Fonds der Chemischen Industrie.

OM9801756

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(39) Koch. J.; Hyla-Kryspin, I.; Gleiter, R.; Klettke, T.; Walther, D. In preparation.