

Articles

Nickel Complexes with Functional Zwitterionic *N,O*-Benzoquinonemonoimine-Type Ligands: Syntheses, Structures, and Catalytic Oligomerization of Ethylene

Qing-Zheng Yang, Anthony Kermagoret, Magno Agostinho, Olivier Siri, and Pierre Braunstein*

Laboratoire de Chimie de Coordination, UMR 7177 CNRS, Institut de Chimie, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex, France

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The zwitterionic *N,N'*-dialkyl-2-amino-5-alcoholate-1,4-benzoquinonemonoiminium derivatives [C₆H₂(←NHCH₂CH₂X)₂(←O)₂] (X = NMe₂, **9**; X = NHet, **10**; X = OMe, **11**), previously prepared from 4,6-diaminoresorcinol by a transamination reaction, and **12** (X = N(CH₂CH₂)₂O) behave as tridentate ligands when reacted with [Ni(acac)₂] to form the corresponding octahedral Ni(II) 2:1 complexes [Ni{C₆H₂(=NCH₂CH₂X)O(=O)(NHCH₂CH₂X)}₂] (**13–16**), respectively. In contrast, ligand **9** reacted

with NiCl₂·6H₂O in a tandemlike manner to afford the stabilized Ni(II) zwitterionic organometalate 1:1 complex [NiCl₂{C₆H₂(=NCH₂CH₂NMe₂)O(=O)(NHCH₂CH₂NHMe₂)}] (**17**). The bonding parameters

of complexes **13**·H₂O·CH₂Cl₂ and **17**, determined by X-ray diffraction, and the conformation of the ligands around the nickel center as well as the supramolecular arrangements are discussed and compared with those of their previously reported Zn(II) analogues. Complexes **13–17** were tested in catalytic ethylene oligomerization with MAO and AlEtCl₂ as cocatalysts. Complex **17** yielded the highest turnover frequencies, with values up to 20 300 and 48 200 mol of C₂H₄/(mol of Ni) h, in the presence of 400 equiv of MAO and 10 equiv of AlEtCl₂, respectively. Selectivities for ethylene dimers were slightly higher when using MAO: 94% (**14** in the presence of 100 equiv of MAO) and 90% (**14** in the presence of 6 equiv of AlEtCl₂). The selectivities for 1-butene within the C₄ fraction were much higher when using MAO as cocatalyst, with values up to 68% (**15** in the presence of 100 equiv of MAO). The fact that **17**, which contains only one tridentate ligand per nickel center, leads to higher activities than **13–16** underlines the importance of the metal center accessibility in the catalytic process.

Introduction

Recent review articles have illustrated the important role played by nickel complexes in the catalytic oligomerization and polymerization of olefins.^{1–3} The competition between olefin-insertion and chain-transfer processes accounts for the occurrence of oligomerization and polymerization reactions, respectively. Obviously, this is a function of a number of parameters, including of course the nature of the ligands and the structure of the precatalyst. With the exception of SHOP-type systems,

which are based on neutral phenyl complexes containing a chelating P,O ligand,^{4–7} activation of the nickel precatalyst by a cocatalyst, such as MAO or AlEtCl₂, is generally required. The choice of the cocatalyst is crucial to the activity and selectivity of the system.^{1–3,8,9} Brookhart et al. have reported very active and selective α-diimine nickel complexes for ethylene polymerization and oligomerization.¹⁰ This work has inspired the synthesis of a number of new nickel complexes with *N,N*-type ligands as precatalysts, using MMAO,¹¹ MAO,¹²

(1) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169–1203.

(2) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283–315.

(3) Speiser, F.; Braunstein, P.; Saussine, L. *Acc. Chem. Res.* **2005**, *38*, 784–793.

(4) (a) Keim, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 235–244. (b) Heinicke, J.; He, M.; Dal, A.; Klein, H. F.; Hetche, O.; Keim, W.; Flörke, U.; Haupt, H.-J. *Eur. J. Inorg. Chem.* **2000**, 431–440. (c) Heinicke, J.; Köhler, M.; Peulecke, N.; He, M.; Kindermann, M. K.; Keim, W.; Fink, G. *Chem. Eur. J.* **2003**, *9*, 6093–6107. (d) Heinicke, J.; Peulecke, N.; Köhler, M.; He, M.; Keim, W. *J. Organomet. Chem.* **2005**, *690*, 2449–2457.

(5) Braunstein, P.; Chauvin, Y.; Mercier, S.; Saussine, L. *C. R. Chim.* **2005**, *8*, 31–38.

(6) Kuhn, P.; Sémeril, D.; Jeunesse, C.; Matt, D.; Neuburger, M.; Mota, A. *Chem. Eur. J.* **2006**, *12*, 5210–5219.

(7) Komon, Z. J. A.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 12379–12380.

(8) Speiser, F.; Braunstein, P.; Saussine, L.; Welter, R. *Organometallics* **2004**, *23*, 2613–2624.

(9) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391–1434.

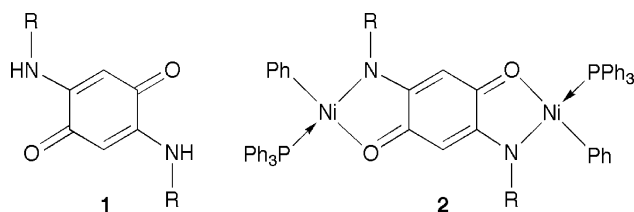
(10) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415.

(11) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005–2007.

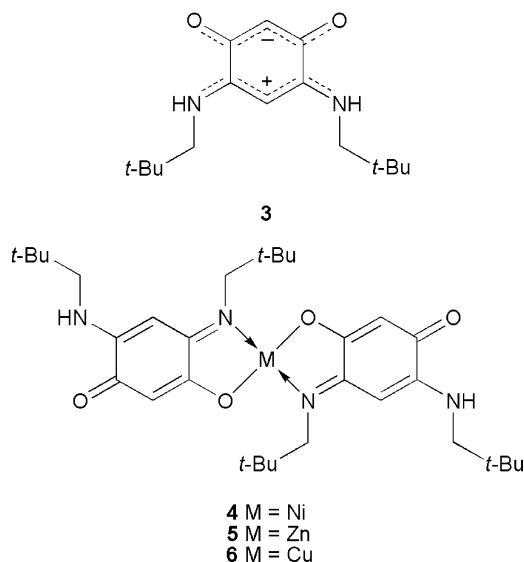
$B(C_6F_5)_3$,¹³ and $Al_2Et_3Cl_3$ ¹⁴ as cocatalysts. Difunctional P,N-type ligands can also lead to very interesting Ni(II) precatalysts, some of them being very active and highly selective for dimerization and trimerization of ethylene in the presence of MAO or $AlEtCl_2$.³

Considerable research effort has been devoted over the past few years to the design of new chelating N,O ligands, and their nickel complexes have shown very high catalytic activity for olefin oligomerization and polymerization.^{15–22} Efficient ethylene polymerization catalysts with N,O-type ligands were developed by Grubbs et al.^{23–25} and Brookhart et al.^{26–28} which are based on salicylaldimine and anilintropone ligands, respectively, and do not require the use of a cocatalyst. Other Ni(II) complexes with N,O chelates catalytically oligomerize ethylene only in the presence of a cocatalyst, such as MAO,^{29,30} $AlEt_3$,³¹ $B(C_6F_5)_3$,³² or ethylaluminum sesquichloride.³³ We have shown that nickel complexes prepared from oxazoline and pyridine alcohols and activated by MAO or $AlEtCl_2$ are very effective and lead to high selectivities for C_4 and C_6 products.³⁴

Although N,O-type ligands have recently been applied in coordination chemistry to the synthesis of porphyrin dimers and oligomers connected by metal ions,^{35,36} only a few examples of mono- or polynuclear metal complexes based on N,O ligands supported by a quinonoid core have been reported.^{37–39} A series of 2,5-disubstituted amino-*p*-benzoquinone ligands of the N,O,N,O type **1** has been used recently by Zhang and co-workers for the preparation of Ni(II) complexes of type **2**, which were active as single-component catalysts in ethylene polymerization.⁴⁰



We recently reported the synthesis and electronic structure of the zwitterionic benzoquinonemonoimine ligand **3** from 4,6-diaminesorcinol dihydrochloride.⁴¹ Assembling of two of these



(12) Chen, L.; Hou, J.; Sun, W.-H. *Appl. Catal., A* **2003**, *246*, 11–16.

(13) Strauch, J. W.; Erker, G.; Kehr, G.; Fröhlich, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2543–2546.

(14) Schareina, T.; Hillebrand, G.; Fuhrmann, H.; Kempe, R. *Eur. J. Inorg. Chem.* **2001**, 2421–2426.

(15) Zuideveld, M. A.; Wehrmann, P.; Roehr, C.; Mecking, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 869–873.

(16) Held, A.; Mecking, S. *Chem. Eur. J.* **2000**, *6*, 4623–4629.

(17) Darenbourg, D. J.; Ortiz, C. G.; Yarbrough, J. C. *Inorg. Chem.* **2003**, *42*, 6915–6922.

(18) Carlini, C.; Isola, M.; Liuzzo, V.; Raspoli Galletti, A. M.; Sbrana, G. *Appl. Catal., A* **2002**, *231*, 307–320.

(19) Zhang, D.; Jin, G.-X.; Hu, N.-H. *Eur. J. Inorg. Chem.* **2003**, 1570–1576.

(20) Li, X.-F.; Li, Y.-S. *J. Polym. Sci., A* **2002**, *40*, 2680–2685.

(21) Pickel, M.; Casper, T.; Rahm, A.; Dambouwy, C.; Chen, P. *Helv. Chim. Acta* **2002**, *85*, 4337–4352.

(22) Novak, B. M.; Tian, G.; Nodono, M.; Boyle, P. *Polym. Mater. Sci. Eng.* **2002**, *86*, 326–327.

(23) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460–462.

(24) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *288*, 1750–1751.

(25) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149–3151.

(26) Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *22*, 250–256.

(27) Hicks, F. A.; Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *22*, 3533–3545.

(28) Brookhart, M.; Jenkins, J. C.; Zhang, L. *Abstracts of Papers; 227th National Meeting of the American Chemical Society, Anaheim, CA, March 28–April 1, 2004; American Chemical Society: Washington, D.C., 2004; POLY-325.*

(29) Sun, W.-H.; Zhang, W.; Gao, T.; Tang, X.; Chen, L.; Li, Y.; Jin, X. *J. Organomet. Chem.* **2004**, *689*, 917–929.

(30) Wang, L.; Sun, W.-H.; Han, L.; Yang, H.; Hu, Y.; Jin, X. *J. Organomet. Chem.* **2002**, *658*, 62–70.

(31) Qian, Y.; Zhao, W.; Huang, J. *Inorg. Chem. Commun.* **2004**, *7*, 459–461.

(32) Chen, Y.; Wu, G.; Bazan, G. C. *Angew. Chem., Int. Ed.* **2005**, *44*, 1108–1112.

(33) Kim, I.; Kwak, C. H.; Kim, J. S.; Ha, C.-S. *Appl. Catal., A* **2005**, *287*, 98–107.

(34) Speiser, F.; Braunstein, P.; Saussine, L. *Inorg. Chem.* **2004**, *43*, 4234–4240.

(35) Richeter, S.; Jeandon, C.; Ruppert, R.; Callot, H. J. *Chem. Commun.* **2001**, 91–92.

benzoquinonemonoimines around the metal center by a metalation reaction using $[M(acac)_2]$ ($M = Ni, Zn, Cu$) afforded complexes **4–6**.⁴¹ Precatalyst **4** was active in ethylene oligomerization and favored the dimerization and trimerization of ethylene when activated with $AlEtCl_2$.⁴²

Therefore, the screening of other functional ligands of type **3** with substituents which could lead, for example, to potentially hemilabile behavior⁴³ should be of particular interest in coordination chemistry and homogeneous catalysis.

The industrial demand for C_4 – C_{20} linear α -olefins has triggered research toward their selective synthesis, and the fast growing need for linear α -olefins in the C_4 – C_{10} range (a ca. 2.5×10^6 tons/year market) explains why their selective formation from ethylene has become a topic of major fundamental and applied importance.⁴⁴ As part of our interest in new ethylene oligomerization Ni(II) catalysts for the production of short-chain oligomers in the presence of only small quantities of $AlEtCl_2$ or MAO, we have extended our preliminary studies

(36) Richeter, S.; Jeandon, C.; Gisselbrecht, J.-P.; Ruppert, R.; Callot, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 6168–6179.

(37) Moriuchi, T.; Watanabe, T.; Ikeda, I.; Ogawa, A.; Hirao, T. *Eur. J. Inorg. Chem.* **2001**, 277–287.

(38) Elduque, A.; Aguilera, F.; Lahoz, F. J.; Lopez, J. A.; Oro, L. A.; Pinillos, M. T. *Inorg. Chim. Acta* **1998**, *274*, 15–23.

(39) Kühlwein, F.; Polborn, K.; Beck, W. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1931–1944.

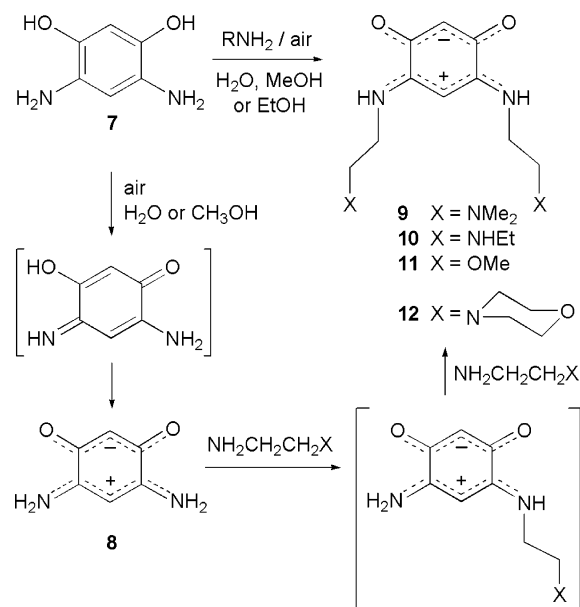
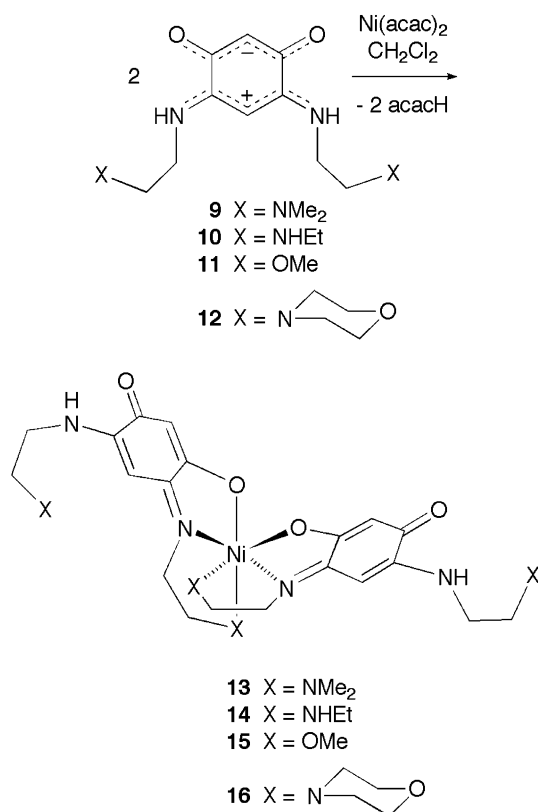
(40) Zhang, D.; Jin, G.-X. *Organometallics* **2003**, *22*, 2851–2854.

(41) Braunstein, P.; Siri, O.; Taquet, J.-p.; Rohmer, M.-M.; Bénard, M.; Welter, R. *J. Am. Chem. Soc.* **2003**, *125*, 12246–12256.

(42) Taquet, J.-p.; Siri, O.; Braunstein, P.; Welter, R. *Inorg. Chem.* **2004**, *43*, 6944–6953.

(43) Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680–699.

(44) Rieger, B.; Saunders Baugh, L.; Kacker, S.; Striegler, S., Eds. *Late Transition Metal Polymerization Catalysis*; Wiley-VCH: Weinheim, Germany, 2003.

Scheme 1. One-Pot Synthesis of the Functional Zwitterions 9–12

Scheme 2. Reactions of Ligands 9–12 Affording the Octahedral Ni(II) Complexes 13–16


on Ni(II) complexes supported by a benzoquinonemonoimine N,O chelate and have now evaluated complexes **13–17**.

Results and Discussion

Ligands and Complexes. The N-substituted, $6\pi + 6\pi$ electron zwitterionic benzoquinonemonoimine ligands **9–11** have been previously obtained from 4,6-diaminoresorcinol dihydrochloride (**7**·2HCl) via the parent zwitterion **8**, by using a new and efficient procedure that involved the first transamination reactions in quinonoid chemistry.^{45,46} The new ligand

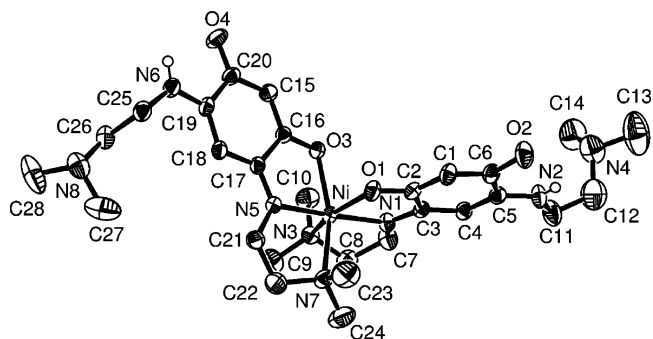


Figure 1. ORTEP view of the crystal structure of **13** in **13**·H₂O·CH₂Cl₂ (ellipsoids drawn at the 50% probability level).

Table 1. Selected Bond Distances (Å) in Complexes **13**·H₂O·CH₂Cl₂ and **17**

	13 ·H ₂ O·CH ₂ Cl ₂	17		13 ·H ₂ O·CH ₂ Cl ₂	17
Ni–N1	2.001(4)	1.975(1)	C2–C1	1.380(6)	1.373(2)
Ni–N3	2.238(4)	2.138(1)	C1–C6	1.407(7)	1.422(2)
Ni–N5	1.989(4)		C6–O2	1.256(6)	1.240(2)
Ni–N7	2.264(4)		N1–C3	1.299(6)	1.295(2)
Ni–O1	2.105(3)	2.142(1)	C3–C4	1.422(6)	1.420(2)
Ni–O3	2.116(3)		C4–C5	1.366(7)	1.371(2)
Ni–C11		2.3337(5)	C5–N2	1.337(6)	1.343(2)
Ni–C12		2.3037(5)	C2–C3	1.506(6)	1.511(2)
O1–C2	1.284(5)	1.289(2)	C5–C6	1.511(7)	1.514(2)

Table 2. Selected Bond Angles (deg) in Complexes **13**·H₂O·CH₂Cl₂ and **17**

	13 ·H ₂ O·CH ₂ Cl ₂	17		13 ·H ₂ O·CH ₂ Cl ₂	17
N5–Ni–N1	175.7(1)		N1–Ni–N3	79.6(2)	81.58(6)
N5–Ni–O3	78.5(1)		O1–Ni–N3	156.9(1)	156.73(5)
N1–Ni–O3	100.6(1)		N3–Ni–N7	101.7(2)	
N5–Ni–O1	97.4(1)		C11–Ni–C12		103.43(2)
N1–Ni–O1	78.3(1)	77.96(5)	C11–Ni–N1		97.78(4)
O1–Ni–O3	86.7(1)		C12–Ni–N1		157.78(5)
N5–Ni–N7	79.3(2)		C12–Ni–O1		98.28(3)
N1–Ni–N7	101.0(2)		C12–Ni–N3		96.47(4)
O3–Ni–N7	156.6(1)		C11–Ni–N3		95.79(4)
O1–Ni–N7	89.0(2)		C11–Ni–O1		98.15(4)
N5–Ni–N3	104.6(2)				

12 has now been prepared in a similar manner (Scheme 1). These ligands react at room temperature with [Ni(acac)₂] in a 2:1 molar ratio of ligand to metal to afford the octahedral complexes **13–16** in high yields (Scheme 2). Monodeprotonation of the ligand results from the basicity of the acac ligand. Owing to their paramagnetism, compounds **13–16** were only characterized by mass spectrometry and elemental analysis. Single crystals of **13**·H₂O·CH₂Cl₂ suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH₂Cl₂ solution of the complex (which contained adventitious water) (see Figure 1 and Tables 1 and 2). Coordination of the pendant amino (ligands **9**, **10**, and **12**) or ether (ligand **11**) function leads to hexacoordinated nickel centers.

As shown in Figure 1, the octahedral geometry around the metal center in the complex **13**·H₂O·CH₂Cl₂ results from the coordination of two tridentate, monometalated ligands, with their two-electron-donor imine nitrogen atoms N(1) and N(5) in mutually trans positions. The covalently bound oxygens O(1) and O(3) are trans to the X donors N(3) and N(7), respectively. The Ni–O and Ni–N bond distances in complex **13** (Table 1) are only slightly shorter than those of its zinc analogue

(45) Yang, Q.-Z.; Siri, O.; Braunstein, P. *Chem. Eur. J.* **2005**, *11*, 7237–7246.

(46) Yang, Q.-Z.; Siri, O.; Braunstein, P. *Chem. Commun.* **2005**, 2660–2662.

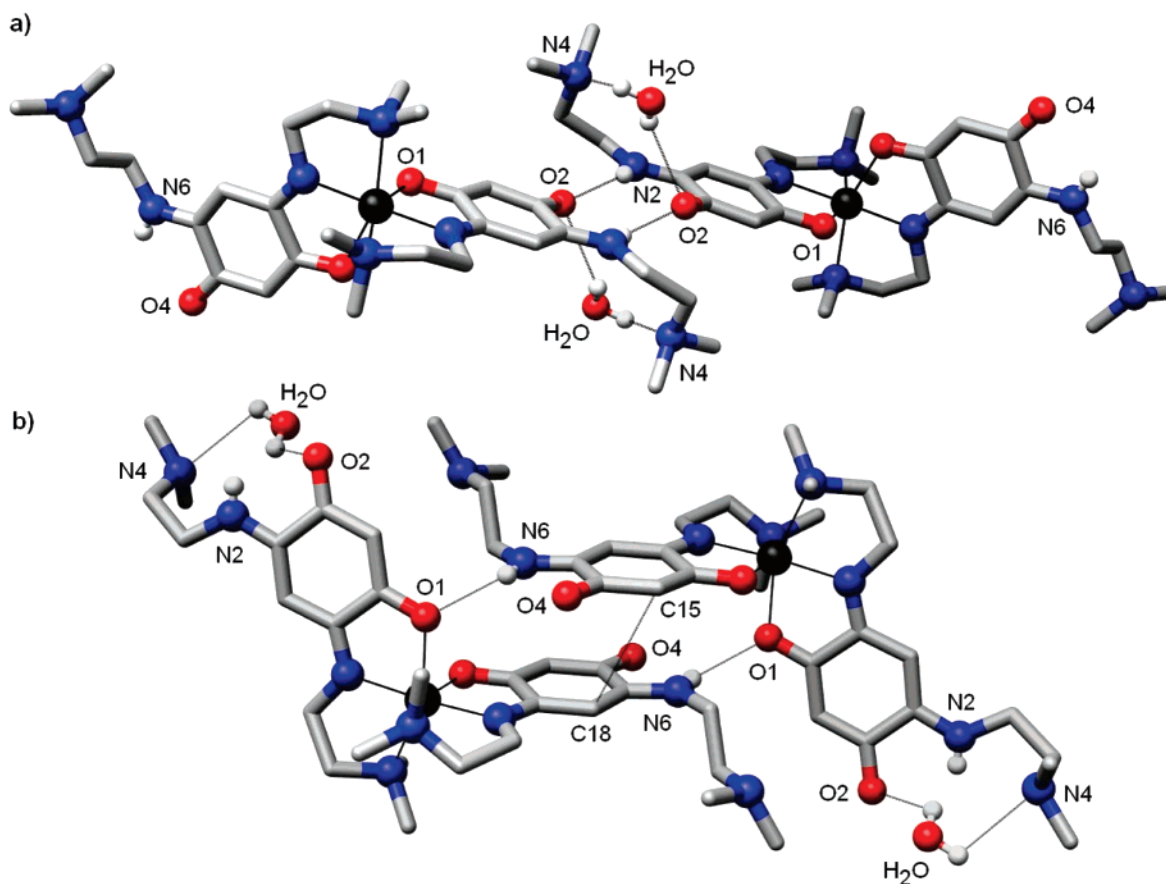


Figure 2. Hydrogen bonding in the complex $13 \cdot H_2O \cdot CH_2Cl_2$ (CH_2Cl_2 solvent molecules omitted for clarity): (a) between N2–H and O2; (b) between N6–H and O1. Color coding: nitrogen, blue; oxygen, red; nickel, black.

(corresponding values (Å): Zn–N1 = 2.021(4), Zn–N3 = 2.330(5), Zn–N5 = 2.037(4), Zn–N7 = 2.442(5), Zn–O1 = 2.123(4), Zn–O3 = 2.134(4)),⁴⁶ which parallels the differences in metal radii (1.246 and 1.333 Å for Ni and Zn, respectively).⁴⁷ Interatomic C–O, C–C, and C–N distances within the quinonemonoimine core of complex **13** indicate an alternation of single and double bonds, which is consistent with a localized π system, as previously observed for the analogous zinc complex,⁴⁶ whereas in the free ligand⁴⁵ and all related crystallographic structures,^{41,42,45,46,48} a highly delocalized π system is present.

Examination of the crystal packing of the complex $13 \cdot H_2O \cdot CH_2Cl_2$ reveals intermolecular N2–H \cdots O2 and N6–H \cdots O1 hydrogen-bonding interactions (N2 \cdots O2 = 2.971(6) Å, N6 \cdots O1 = 2.897(6) Å), which lead to a one-dimensional wavelike chain arrangement in the solid-state (Figures 2 and 3). This arrangement also allows stabilizing π – π interactions between quinone rings, with a C15 \cdots C18 distance of 3.650(6) Å. A similar arrangement was also observed in its Zn(II) analogue.^{45,46} However, in the present case, the complex crystallized with a molecule of water and of dichloromethane. The H₂O molecules interact through hydrogen bonding, with O2 \cdots O(H₂O) and N4 \cdots O(H₂O) distances of 2.994(15) and 2.954(12) Å, respectively. The CH₂Cl₂ molecules are placed between the wavelike chains, one of their C–H bonds interacting with O4 (O4 \cdots C29(CH₂Cl₂) = 3.23(2) Å, O4–H29A–C29 = 155°).

When ligand **9** was reacted with NiCl₂·6H₂O in a 1:1 molar ratio at room temperature in MeOH, it afforded the mononuclear complex **17** (Scheme 3). In contrast to the fate of the acac ligand in Scheme 2, both chloride ligands remain coordinated to the nickel center in **17**. The molecular structure of this complex was determined by X-ray diffraction (Figure 4 and Tables 1 and 2). Like its Zn(II) analogue,⁴⁵ **17** presents a zwitterionic structure, where the negative charge of the metalate moiety is balanced by the ammonium cation resulting from an intramolecular proton shift.

This zwitterionic complex contains only one tridentate ligand per nickel center, and the pentacoordination about the metal results in a slightly distorted square-based-pyramidal geometry (Figure 4). The base is formed by the three ligand donor sites (N1, N3, and O1) and Cl2, while Cl1 completes the coordination sphere in the apical position of the pyramid. The nickel is at a distance of 0.3536(3) Å from the mean plane passing through N1, N3, O1, and Cl2.

As observed with its Zn(II) analogue,⁴⁵ complex **17** forms in the solid state a pseudodimer which is stabilized by the N4–H \cdots O1 interaction (N4 \cdots O1 = 2.810(2) Å) and π – π stacking with a C1 \cdots C4 distance of 3.542(3) Å (Figure 5). These pseudo-dimers are in turn organized along chains, in an alternate A–A'–A–A' manner, where dimer A is rotated by 88.92(4)° around the chain axis with respect to dimer A' (Figure 6). There are no short contacts between these pseudo-dimers.

Catalytic Oligomerization of Ethylene. The precatalysts **13**–**17** have been tested in the presence of variable amounts of AlEtCl₂ or MAO as cocatalyst and showed high activities for the dimerization and trimerization of ethylene (Tables 3 and 4). The results were compared with those obtained with NiCl₂–

(47) Holleman, A. F.; Wiberg, E. *Holleman-Wiberg Lehrbuch der Anorganischen Chemie*, 91st–100th eds.; Walter de Gruyter: Berlin, 1985; pp 1152–1156.

(48) Siri, O.; Braunstein, P. *Chem. Commun.* **2002**, 208–209.

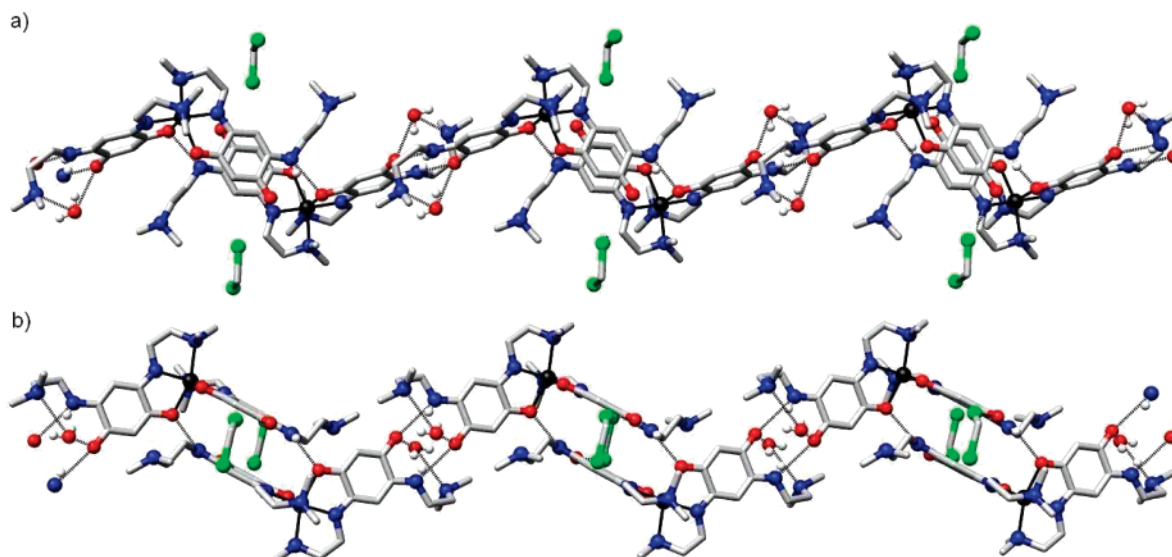
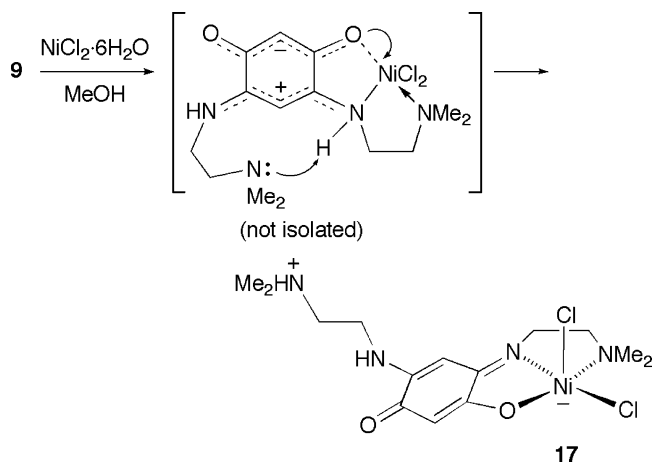


Figure 3. Views of the supramolecular array generated by $13 \cdot \text{H}_2\text{O} \cdot \text{CH}_2\text{Cl}_2$ in the solid state: (a) top view; (b) side view. Color coding: nitrogen, blue; oxygen, red; chloride, green; nickel, black.

Scheme 3. Reaction of Ligand 9 with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ Affording the Pentacoordinated Ni(II) Complex 17^a



^a The negative charge shown for clarity on the Ni(II) center is, of course, partially delocalized on the ligands.

(PCy_3)₂, a typical α -olefin dimerization catalyst^{49,50} (Figures 7–11). We felt it would be interesting to determine the fractions of the different C₆ oligomers formed by chain growth or by reinsertion of 1-butene or 2-butene (Tables 5 and 6). Depending on the nature of their insertion (2,1- or 1,2-insertion) and on which C–H bond undergoes agostic interaction with the metal,^{51–54} two schemes can explain the formation of 2-hexene, 3-hexene, and 2-ethylbut-1-ene from 1-butene (Scheme 4) and the formation of 3-methylpent-2-ene and 3-methylpent-1-ene from 2-butene (Scheme 5). 1-Hexene is formed by a chain growth mechanism, and its Ni-catalyzed isomerization leads to 2-hexene and 3-hexene.⁵⁵

(49) Knudsen, R. D. *Prepr.-Am. Chem. Soc., Div. Petrol. Chem.* **1989**, 572–576.

(50) Commereuc, D.; Chauvin, Y.; Leger, G.; Gaillard, J. *Rev. Inst. Fr. Pet.* **1982**, 37, 639–649.

(51) Tempel, D. J.; Brookhart, M. *Organometallics* **1998**, 17, 2290–2296.

(52) Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, 18, 65–74.

(53) Gottfried, A. C.; Brookhart, M. *Macromolecules* **2003**, 36, 3085–3100.

(54) Zhao, W.; Qian, Y.; Huang, J.; Duan, J. *J. Organomet. Chem.* **2004**, 689, 2614–2623.

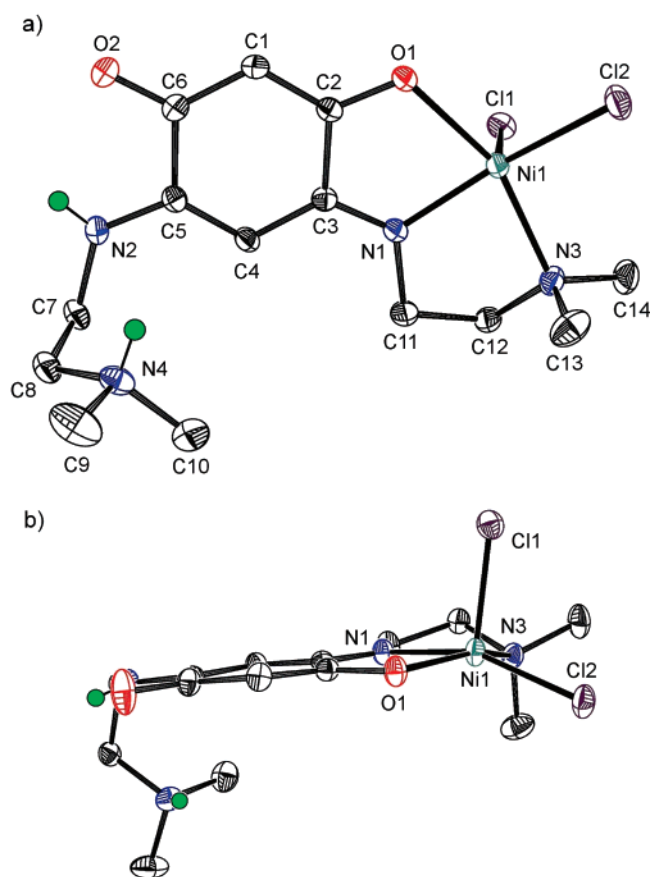


Figure 4. ORTEP view of the structure of **17** (ellipsoids drawn at the 50% probability level): (a) view from the bottom of the square-based pyramid; (b) side view. The C–H atoms are not shown.

A comparison of the various catalytic results should indicate the influence of (i) the nature of the donor function in the complexing ligand arm, (ii) the increase in metal coordination number resulting from the presence of the complexing arm, by comparison with the properties of **4**, (iii) the metal coordination geometry, (iv) the nature of the cocatalyst, and (v) the lifetime of the catalyst.

(i) Influence of the Donor Function in the Arm. Complexes **13–16** display hexacoordinate geometry around the metal

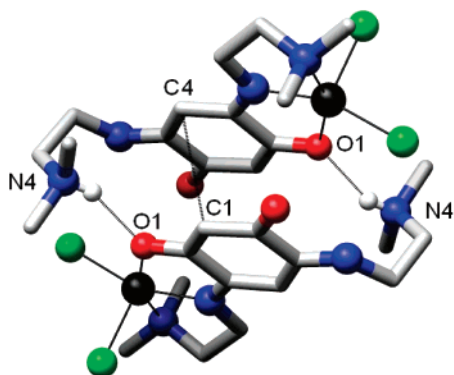


Figure 5. Hydrogen bonding in the pseudo-dimers formed by the zwitterionic Ni(II) complex **17** in the solid state. Color coding: nitrogen, blue; oxygen, red; chloride, green; nickel, black.

center, with the ligand coordinating arm endowed with different donor functions. Precatalysts **13–15** afforded similar results with AlEtCl_2 , with turnover frequency (TOF) values between 24 300 and 24 400 or between 35 600 and 37 200 mol of $\text{C}_2\text{H}_4/(\text{mol of Ni h})$, when 6 or 10 equiv of cocatalyst was used, respectively (Table 3). Complex **16** showed a slightly lower activity (23 000 mol of $\text{C}_2\text{H}_4/(\text{mol of Ni h})$ with 10 equiv of AlEtCl_2). The selectivities for C_4 olefins observed with **13–16** were very similar and were close to 89% or 82% in the presence of 6 or 10 equiv of AlEtCl_2 , respectively. However, the selectivities for α -butene were lower than 10%.

With MAO as cocatalyst, the activities and selectivities of **13–15** were of similar orders of magnitude. Their activities were in the range 1300–2900 mol of $\text{C}_2\text{H}_4/(\text{mol of Ni h})$ with 100 equiv of MAO and 7400–10 300 mol of $\text{C}_2\text{H}_4/(\text{mol of Ni h})$ with 200 equiv, and the activity of **13** was found to be 15 400 mol of $\text{C}_2\text{H}_4/(\text{mol of Ni h})$ in the presence of 400 equiv of MAO (Table 4). The selectivities for C_4 olefins were around 93% with 100 equiv and 85% for 200 equiv of MAO. With **13–15**, the selectivity for 1-butene was up to 68% with 100 equiv of MAO and 47% with 200 equiv. Under these conditions, precatalyst **16** showed a higher activity but a lower selectivity in C_4 products and 1-butene in comparison to **13–15**.

A comparison between the four different functions available in the complexing arm shows that, with both cocatalysts, the tertiary amine (precatalyst **13**), the secondary amine (precatalyst **14**), and the ether function (precatalyst **15**) led to similar catalytic results in ethylene oligomerization but the morpholine function (precatalyst **16**) led to a less active catalyst with AlEtCl_2 but a more active catalyst with MAO.

(ii) Influence of the Ligand Coordinating Arm. In contrast to **4**, complexes **13–17** have a coordinating arm which could display either static chelation or potentially hemilabile behavior and therefore influence the catalytic results. A comparison of the results obtained with **4** and **13–16**, in which the nickel center is coordinated by two ligands, is provided in Table 3. The activity of **4** (28 500 and 45 000 mol of $\text{C}_2\text{H}_4/(\text{mol of Ni h})$ with 6 and 10 equiv of AlEtCl_2 , respectively) and its selectivity for 1-butene were higher (14%) than those of **13–16**. However, the selectivity for C_4 olefins was only 51% with **4** but up to 90% with **13–16**. This suggests that the presence of the coordinating arm in complexes **13–16** disfavors both the insertion of ethylene and the reinsertion mechanism which leads to the C_6 oligomers.

(iii) Influence of the Coordination Geometry of the Metal.

One of the objectives of this study was to determine the influence on the catalytic properties of hexacoordination in complexes with two tridentate benzoquinonemonoimine ligands and of pentacoordination in complexes containing only one benzoquinonemonoimine ligand and two chlorides. This can be done by comparing the performances of compounds **13** and **17**. Precatalyst **17** led to higher activities than **13** with AlEtCl_2 or MAO as cocatalyst, up to 48 200 mol of $\text{C}_2\text{H}_4/(\text{mol of Ni h})$ with AlEtCl_2 and 20 300 mol of $\text{C}_2\text{H}_4/(\text{mol of Ni h})$ with MAO (Table 4). In the presence of MAO or AlEtCl_2 , the most active precatalyst in the series was **17**. The difference in activity between **17** and **13** could be due to an easier generation of the active species by nickel alkylation in the former case than with **13**, where it probably requires the loss of a chelating N,O ligand. However, the selectivity of **17** for C_4 products and for 1-butene was lower than with **13**.

The catalyst ability to reinsert the primary C_4 products has a clear impact on product selectivity (Schemes 4 and 5). Data in Table 5 show that the fraction of branched C_6 oligomers formed from 2-butene was ca. 59% for **17** and ca. 53% for **13** with AlEtCl_2 . A similar observation was made with MAO as cocatalyst. Consequently, precatalyst **17**, which is more active than **13** and reinserts 2-butene more readily than **13** to form C_6 products, leads to a lower selectivity for butenes.

(iv) Influence of the Cocatalyst. The use of AlEtCl_2 or MAO as cocatalyst influenced the catalytic results presented in Tables 3 and 4: the activities (up to 48 200 mol of $\text{C}_2\text{H}_4/(\text{mol of Ni h})$) were higher with AlEtCl_2 as cocatalyst than with MAO, but MAO generally led to a higher selectivity for C_4 olefins (94% for **14**, with 100 equiv of MAO). The precatalysts activated by AlEtCl_2 afforded strongly isomerizing systems so that the fraction of 2-butene is very high (up to 95%). The high selectivity for C_4 olefins is consistent with the more difficult reinsertion of 2-butene to form C_6 oligomers compared to 1-butene. In contrast, MAO associated with **13–17** favored chain growth, as indicated by the percentages of 1-butene (up to 68%) and 1-hexene (up to 21%) within their respective fractions, and of C_8 oligomers (up to 9%).

The amount of cocatalyst used significantly influences the catalytic results, particularly with MAO. Increasing the amounts of MAO resulted in increased activity for **13–17** but decreased selectivity in both 1- and 2-butenes (Table 4). Reinsertion of 1-butene results in the formation of higher oligomers (the selectivity for 1-butene decreased from 49% to 24% with **13**, for example). The increased percentage of C_6 oligomers from 2-butene (from 11% with 100 equiv of MAO to 32% with 400 equiv with **13**, for example) shows that the reinsertion of 2-butene is also favored by increasing amounts of MAO.

(v) Lifetime of the Catalyst. To study the lifetime of the catalysts, complex **17**, the most active precatalyst, was tested with 10 equiv of AlEtCl_2 with a reaction time increased to 200 min. The robustness of the catalyst was indicated by a constant activity during catalysis (the consumption of C_2H_4 was constant, no plateau of activity was observed, and the final activity was 20 500 mol of $\text{C}_2\text{H}_4/(\text{mol of Ni h})$). Selectivities were similar to those observed under standard conditions (Table 3).

Conclusion

New Ni(II) complexes have been synthesized with tridentate zwitterionic benzoquinonemonoimine ligands. The reaction of

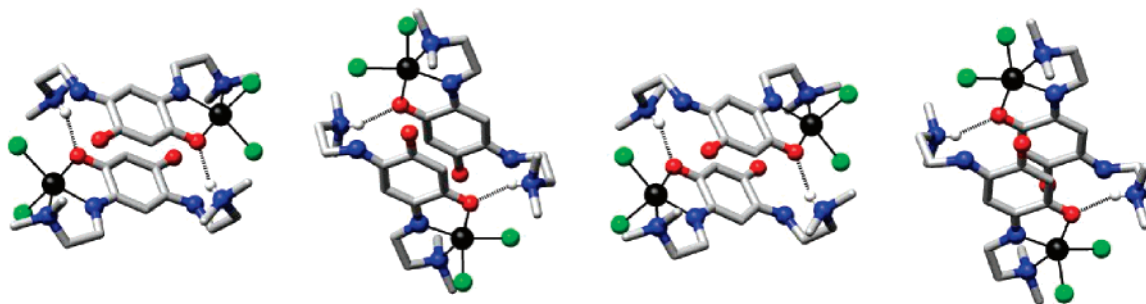


Figure 6. View of the array generated by the pseudo-dimers formed by the zwitterionic Ni(II) complex **17** in the solid state. Color coding: nitrogen, blue; oxygen, red; chloride, green; nickel, black.

Table 3. Comparative Catalytic Data for Complexes 13–17 in the Oligomerization of Ethylene with AlEtCl₂ as Cocatalyst^{a,b}

	amt of AlEtCl ₂ (equiv)	selectivity (mass %)		productivity (g of C ₂ H ₄ /((g of Ni) h))	TOF (mol of C ₂ H ₄ /((mol of Ni) h))	amt of α-olefin (C ₄) (mol %)	k _α ^c
		C ₄	C ₆				
13	6	88	12	11 700	24 400	5.8	<0.10
13	10	82	18	17 700	37 200	5.3	0.15
14	6	90	10	11 600	24 300	9.4	<0.10
14	10	80	20	17 500	36 900	6.3	0.16
15	6	89	11	11 600	24 300	8.3	<0.10
15	10	80	20	17 000	35 600	4.6	0.16
16	10	83	16	10 900	23 000	7.1	0.13
17	6	72	28	20 600	43 300	4.5	0.26
17	10	76	23	23 000	48 200	5.7	0.20
17^d	10	76	24	10 000	20 500	6.2	0.22
4⁴²	6	49	45	13 500	28 500	14.0	0.60
4	10	51	43	21 500	45 000	7.0	0.57
ref ^e	6	59	34	27 600	57 800	11.2	0.38
ref	10	65	31	24 400	51 500	9.8	0.32

^a Conditions: $T = 30\text{ }^{\circ}\text{C}$, 10 bar of C₂H₄, 35 min, 4×10^{-5} mol of Ni complex, solvent 12 mL of chlorobenzene and 3 mL of cocatalyst solution in toluene, or 10 mL of chlorobenzene and 5 mL of cocatalyst solution in toluene, for 6 or 10 equiv of AlEtCl₂, respectively. ^b No C₈–C₁₀ oligomers were detected. ^c $k_{\alpha} = (\text{mol of hexenes})/(\text{mol of butenes})$. ^d Reaction time 200 min. ^e Reference: NiCl₂(PCy₃)₂.

Table 4. Comparative Catalytic Data for Complexes 13–17 in the Oligomerization of Ethylene with MAO as Cocatalyst^{a,b}

	amt of MAO (equiv)	selectivity (mass %)			productivity (g of C ₂ H ₄ /((g of Ni) h))	TOF (mol of C ₂ H ₄ /((mol of Ni) h))	amt of α-olefin (C ₄) (mol %)	k _α ^c
		C ₄	C ₆	C ₈				
13	100	92	7	<1	1400	2900	49	<0.10
13	200	87	14	2	3600	7600	47	0.11
13	400	65	29	5	7300	15400	24	0.30
14	100	94	5	<1	600	1300	61	<0.10
14	200	86	12	2	3500	7400	45	0.11
15	100	93	6	<1	1300	2700	68	<0.10
15	200	82	17	1	4800	10300	37	0.14
16	100	86	12	2	2400	5000	50	<0.10
16	200	69	26	5	6100	13000	28	0.25
16	400	63	29	7	8800	18500	22	0.32
17	100	77	21	2	5500	11600	27	0.18
17	200	71	24	5	7400	16100	22	<0.10
17	400	55	35	9	9700	20300	19	0.42
ref ^d	200	74	18	8	600	1200	76	0.16
ref	400	70	26	4	3000	6400	72	0.24

^a Conditions: $T = 30\text{ }^{\circ}\text{C}$, 10 bar of C₂H₄, 35 min, 4×10^{-5} mol of Ni complex; solvent 12 mL of chlorobenzene and 4, 8, or 16 mL of cocatalyst solution in toluene for 100, 200, or 400 equiv of MAO, respectively. ^b Traces of C₁₀ oligomers were detected when using 400 equiv of MAO. ^c $k_{\alpha} = (\text{mol of hexenes})/(\text{mol of butenes})$. ^d Reference: NiCl₂(PCy₃)₂.

2 equiv of the ligands **9**–**12** with Ni(acac)₂ led to the formation of **13**–**16**, respectively, with a hexacoordinated nickel center, whereas the reaction of 1 equiv of **9** with NiCl₂·6H₂O afforded the zwitterionic complex **17** with a pentacoordinated nickel center. Obviously, the higher basicity of the acac ligand compared to that of chloride is responsible for the difference observed as a function of the Ni(II) precursor.

The precatalysts **13**–**17** have been tested in the oligomerization of ethylene with different amounts of AlEtCl₂ or MAO as cocatalyst. The results showed that AlEtCl₂ led to more active and less selective systems in α-olefins than did MAO. Increasing amounts of MAO or AlEtCl₂ as cocatalyst resulted in more active but less selective systems.

The influence of the complexing arm of **9**–**12** was evaluated by comparing **4** with **13**–**16**. It was found that its presence led to lower activities but better selectivity in C₄ oligomers because it disfavored butene reinsertion. The comparison of **13**–**16** showed that the different complexing functions of the arm have no significant consequences on the catalytic results. Only **16** showed higher activities and lower selectivities with MAO as cocatalyst and lower activities with AlEtCl₂ as cocatalyst than **13**–**15**.

The influence of the geometry of the complexes has been determined by the comparison between **13** and **17**, and it was found that pentacoordination favored the insertion of olefins and led to higher activity but lower selectivity.

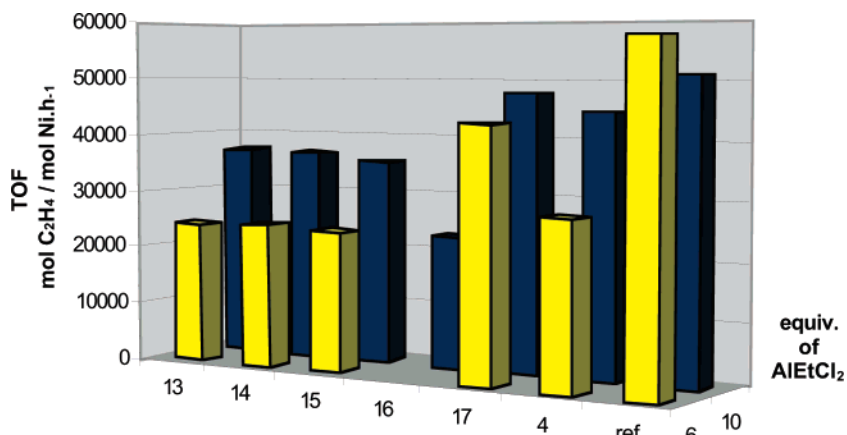


Figure 7. Catalytic activities of the complexes **13–17** and **4** in the oligomerization of ethylene using AlEtCl₂ as cocatalyst, Ref: NiCl₂(PCy₃)₂.

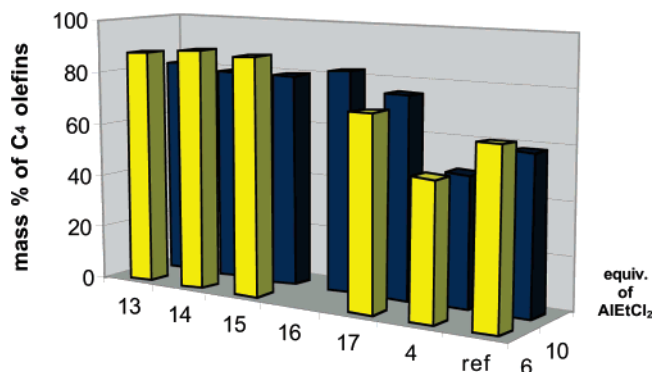


Figure 8. Selectivity of the complexes **13–17** and **4** for C₄ compounds (1-butene and 2-butene), NiCl₂(PCy₃)₂ was used as the reference.

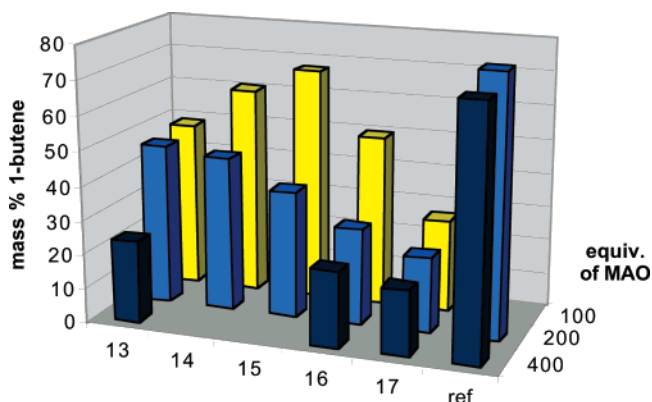


Figure 10. Selectivity of the complexes **13–17** for 1-butene within the C₄ fraction. NiCl₂(PCy₃)₂ was used as the reference.

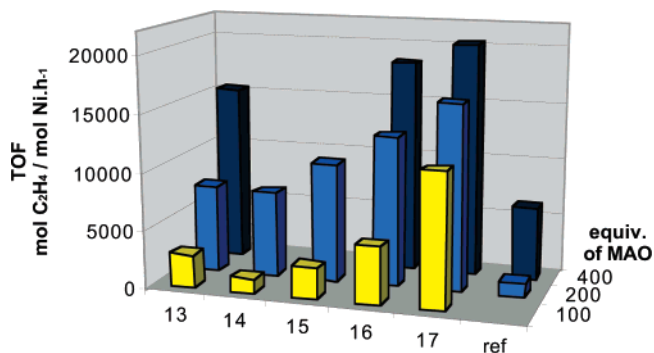


Figure 9. Catalytic activities of the complexes **13–17** in the oligomerization of ethylene using MAO as cocatalyst. NiCl₂(PCy₃)₂ was used as the reference.

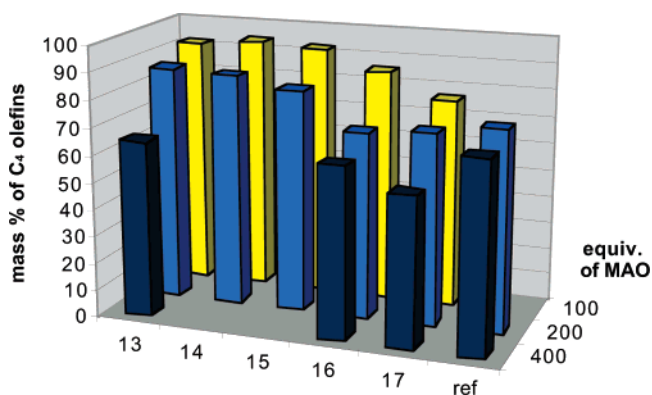


Figure 11. Selectivity of the complexes **13–17** for C₄ olefins (1-butene and 2-butene). NiCl₂(PCy₃)₂ was used as the reference.

Experimental Section

General Considerations. All solvents were dried and freshly distilled under nitrogen prior to use using common techniques. All manipulations were carried out using Schlenk techniques. ¹H (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded on a Bruker AC300 instrument. MALDI-TOF mass spectra were recorded on a Biflex III Bruker mass spectrometer. Elemental analyses were performed by the Service de Microanalyse, Université Louis Pasteur (Strasbourg, France). 4,6-Diaminoresorcinol dihydrochloride and the functional amines were commercially available. Ligands **9–11** have been prepared according to the literature.^{45,46}

Ligand 12. To a stirred solution of diaminoresorcinol dihydrochloride (2.13 g, 10 mmol) in water (30 mL) was added 4-(2-aminoethyl)morpholine (9.76 g, 75 mmol), and the reaction mixture was extracted with CH₂Cl₂ after 2 h. The organic layer was

collected, dried with MgSO₄, filtered, and concentrated to ca. 30 mL. Pentane was added to the solution, and the pale gray precipitate was isolated by filtration. Yield: 74%. MS (MALDI-TOF⁺): *m/z* 365.2 [*M* + 1]⁺. ¹H NMR (300 MHz, CDCl₃): δ 2.50 (t, ³*J* = 4.5 Hz, 8H, NCH₂CH₂O), 2.71 (t, ³*J* = 6.1 Hz, 4H, NHCH₂CH₂N), 3.42 (t, ³*J* = 6.1 Hz, 4H, NHCH₂), 3.73 (t, ³*J* = 4.5 Hz, 8H, OCH₂), 5.10 (s, 1H, N=C–CH), 5.44 (s, 1H, O=C–CH), 8.48 (br s, 2H, NH). ¹³C NMR (75 MHz, CDCl₃) δ 39.48 (s, NCH₂CH₂O), 53.29 (s, NHCH₂CH₂N), 55.42 (s, NHCH₂), 66.84 (s, OCH₂), 81.27 (s, N=C–C), 99.01 (s, O=C–C), 156.79 (s, N=C), 172.23 (s, O=C). Anal. Calcd for C₁₈H₂₈N₄O₄·0.5H₂O: C, 57.89; H, 7.83; N, 15.00. Found: C, 57.75; H, 7.80; N, 15.36.

Complex 13. Ligand **9** (1.12 g, 4.0 mmol) was dissolved in dichloromethane (200 mL), and 0.5 equiv of solid [Ni(acac)₂] (0.55 g, 2.0 mmol) was then added to the solution in one portion. After

Table 5. Catalytic Data and Distribution of the C₆ Alkenes for Complexes 13–17 in the Oligomerization of Ethylene with AlEtCl₂ as Cocatalyst^a

	amt of AlEtCl ₂ (equiv)	selectivity (mass %)			
		1-hexene	linear C ₆ ^b	C ₆ ^c from 1-butene	C ₆ ^d from 2-butene
13	6	0	39	9	52
13	10	0	39	7	54
14	6	0	42	13	45
14	10	0	43	7	50
15	6	0	46	11	43
15	10	0	43	6	51
16	10	<1 ^e	46	3	50
17	6	0	36	6	58
17	10	0	36	4	60

^a Conditions: $T = 30\text{ }^{\circ}\text{C}$, 10 bar of C₂H₄, 35 min, 4×10^{-5} mol of Ni complex, solvent 12 mL of chlorobenzene and 3 mL of cocatalyst solution in toluene or 10 mL chlorobenzene and 5 mL of cocatalyst solution in toluene, for 6 or 10 equiv of AlEtCl₂, respectively. ^b Sum of 3-*cis*-hexene, 3-*trans*-hexene, 2-*cis*-hexene, and 2-*trans*-hexene. ^c Corresponds to 2-ethyl-1-butene. ^d Sum of 3-methyl-1-pentene, 3-methyl-2-*cis*-pentene, and 3-methyl-2-*trans*-pentene. ^e Only in this case was 1-hexene detected.

Table 6. Catalytic Data for Complexes 13–17 and Distribution of the C₆ Alkenes in the Oligomerization of Ethylene with MAO as Cocatalyst^a

	amt of MAO (equiv)	selectivity (mass %)			
		1-hexene	linear C ₆ ^b	C ₆ ^c from 1-butene	C ₆ ^d from 2-butene
13	100	18	58	13	11
13	200	8	61	12	19
13	400	5	50	13	32
14	100	20	54	12	14
14	200	9	59	12	20
15	100	21	58	12	9
15	200	7	57	13	23
16	100	10	57	13	20
16	200	6	52	12	30
16	400	4	51	11	34
17	100	5	54	12	29
17	200	4	50	11	34
17	400	4	50	11	35

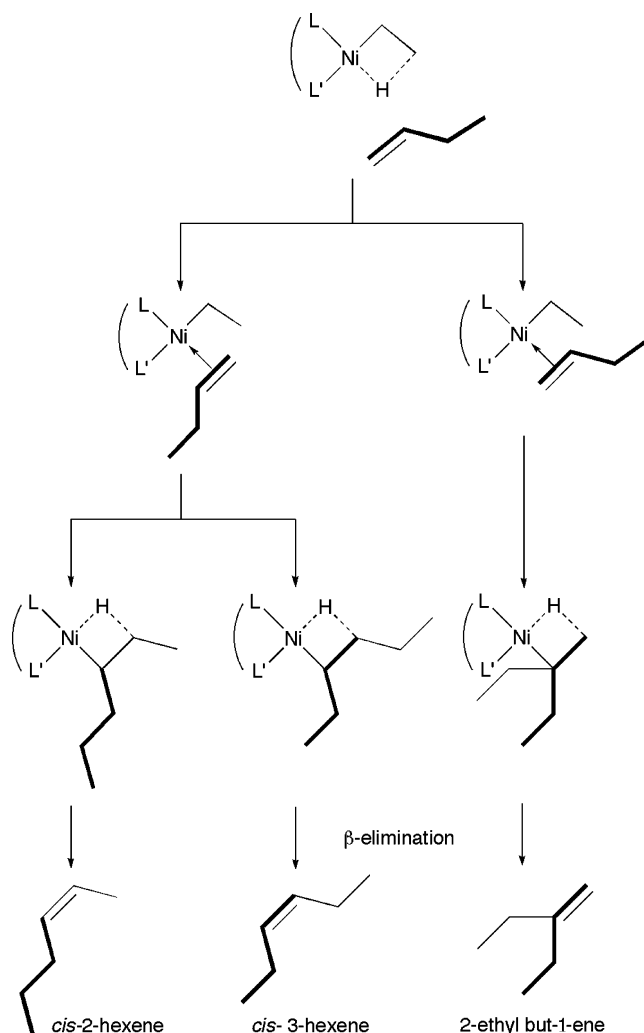
^a Conditions: $T = 30\text{ }^{\circ}\text{C}$, 10 bar of C₂H₄, 35 min, 4×10^{-5} mol of Ni complex; solvent 12 mL of chlorobenzene and 4, 8, or 16 mL of cocatalyst solution in toluene for 100, 200, or 400 equiv of MAO, respectively. ^b Sum of 3-*cis*-hexene, 3-*trans*-hexene, 2-*cis*-hexene, and 2-*trans*-hexene. ^c Corresponds to 2-ethyl-1-butene. ^d Sum of 3-methyl-1-pentene, 3-methyl-2-*cis*-pentene, and 3-methyl-2-*trans*-pentene.

the solution was stirred at room temperature for 3 h, the solvent was concentrated to ca. 20 mL under vacuum and the red crystalline complex **13** was obtained by precipitation from a mixture of dichloromethane and pentane. Yield: 92%. MS (MALDI-TOF⁺): m/z 617.3 [$M + 1$]⁺. Anal. Calcd for C₂₈H₄₆N₈NiO₄·H₂O·CH₂Cl₂: C, 48.35; H, 7.00; N, 15.56. Found: C, 48.65; H, 7.12; N, 15.78.

Complex 14. The synthetic procedure was similar to that described for complex **13**, but using ligand **10** instead of **9**. Yield: 88%. MS (MALDI-TOF⁺): m/z 617.3 [$M + 1$]⁺. Anal. Calcd for C₂₈H₄₆N₈NiO₄·0.5H₂O·0.5CH₂Cl₂: C, 51.18; H, 7.23; N, 16.75. Found: C, 51.06; H, 7.28; N, 17.04.

Complex 15. The synthetic procedure was similar to that described for complex **13**, but using ligand **11** instead of **9**. Yield: 91%. MS (MALDI-TOF⁺): m/z 565.2 [$M + 1$]⁺. Anal. Calcd for C₂₄H₃₄N₄NiO₈: C, 51.00; H, 6.06; N, 9.91. Found: C, 50.91; H, 6.03; N, 9.85.

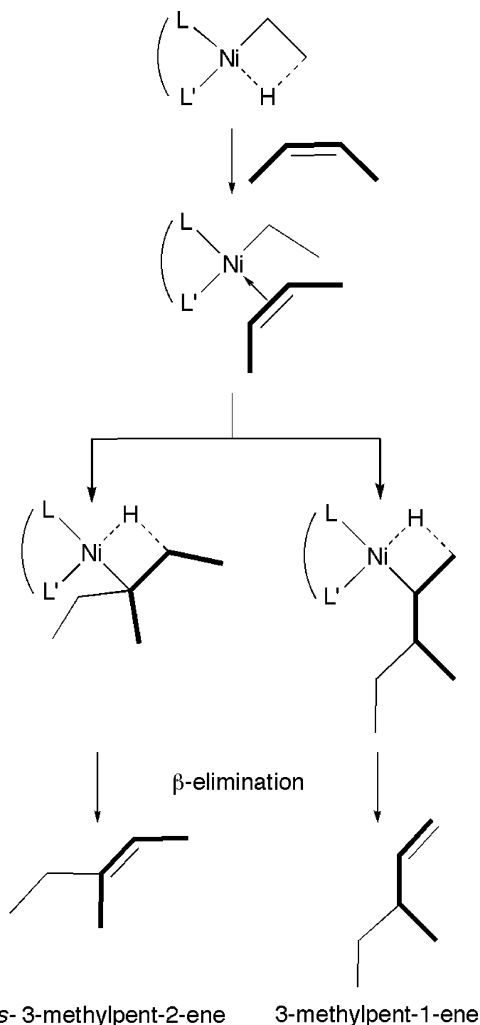
Complex 16. The synthetic procedure was similar to that described for complex **13**, but using ligand **12** instead of **9**. Yield: 93%. MS (MALDI-TOF⁺): m/z 785.3 [$M + 1$]⁺. Anal. Calcd for C₃₆H₅₄N₈NiO₈·0.5H₂O: C, 54.42; H, 6.98; N, 14.10. Found: C, 54.37; H, 7.03; N, 13.91.

Scheme 4. Products Resulting from the Reinsertion of 1-Butene^a

^a The stereochemical information is not illustrated: agostic interactions with diastereotopic CH₂ protons afford the *cis* or *trans* isomers.

Complex 17. To a solution of ligand **9** (0.28 g, 1.0 mmol) in methanol (30 mL) was added 1 equiv of NiCl₂·6H₂O (0.24 g, 1.0 mmol), and the reaction mixture was stirred for 3 h. Complex **17** was obtained as a purple crystalline solid by slow diffusion of ether into the reaction mixture. Yield: 71%. MS (MALDI-TOF⁻): m/z 409.1 [$M - 1$]⁻. Anal. Calcd for C₁₄H₂₄Cl₂N₄NiO₂: C, 41.02; H, 5.90; N, 13.67. Found: C, 40.81; H, 6.11; N, 13.33.

Oligomerization of Ethylene. All catalytic reactions were carried out in a magnetically stirred (900 rpm) 145 mL stainless steel autoclave. A 125 mL glass container was used to protect the inner walls of the autoclave from corrosion. All catalytic tests were started at 30 °C, and no cooling of the reactor was done during the reaction. After injection of the catalytic solution and of the cocatalyst under a constant low flow of ethylene, the reactor was pressurized to 10 bar. A temperature increase was observed which resulted solely from the exothermicity of the reaction. The 10 bar working pressure was maintained during the experiments through a continuous feed of ethylene from a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. In all of the catalytic experiments 4×10^{-2} mmol of Ni complex was used. The oligomerization products and remaining ethylene were only collected from the reactor at the end of the catalytic experiment. At the end of each test (35 min) a dry ice bath, and in the more exothermic cases also liquid N₂, was used to rapidly cool the reactor, thus stopping the reaction. When the inner temperature reached 0

Scheme 5. Pentenes Resulting from the Reinsertion of 2-Butene^a

^a The stereochemical information is not illustrated.

°C, the ice bath was removed, allowing the temperature to slowly rise to 10 °C. The gaseous phase was then transferred into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated, for GC analysis. The products in the reactor were hydrolyzed in situ by the addition of ethanol (1 mL), transferred into a Schlenk flask, and separated from the metal complexes by trap-to-trap evaporation (20 °C, 0.3 mmHg) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid any loss of product. For GC analyses, 1-heptene was used as an internal reference. When AlEtCl₂ was used as cocatalyst, depending on the amount used (6 or 10 equiv), the required quantity of Ni(II) complex was dissolved in 12 or 10 mL of chlorobenzene, respectively, and injected into the reactor. The cocatalyst solution, 3 or 5 mL corresponding to 6 or 10 equiv, respectively, was then added. Therefore, the total volume of the solution inside the reactor, for all the tests performed with AlEtCl₂, was 15 mL. In the cases where MAO was used as cocatalyst, the Ni(II) complex was always dissolved in 12 mL of chlorobenzene, and after injection of this solution, the desired amount of cocatalyst was added. The total volume of the solution inside the reactor at the beginning of each test was therefore dependent on the amount of cocatalyst used. Total volumes of 16, 20, and 28 mL correspond to 100, 200, and 400 equiv of MAO, respectively.

Table 7. Crystal Data and Details of the Structure Determination for Compounds **13**·H₂O·CH₂Cl₂ and **17**

	13 ·H ₂ O·CH ₂ Cl ₂	17
formula	C ₂₈ H ₄₆ N ₈ NiO ₄ · H ₂ O·CH ₂ Cl ₂	C ₁₄ H ₂₄ Cl ₂ N ₄ NiO ₂
<i>M_r</i>	720.38	409.98
cryst syst	triclinic	monoclinic
space group	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	12.104(5)	7.5710(10)
<i>b</i> (Å)	12.574(5)	9.900(10)
<i>c</i> (Å)	12.884(5)	23.534 (4)
α (deg)	78.262 (5)	
β (deg)	70.304(5)	104.10 (5)
γ (deg)	81.282 (5)	
<i>V</i> (Å ³)	1800.2(12)	1710.8(6)
<i>Z</i>	2	4
ρ _{calcd} (g cm ⁻³)	1.329	1.592
μ (mm ⁻¹)	0.734	1.460
<i>T</i> (K)	173(2)	173(2)
λ (Å)	0.710 69	0.710 70
θ _{max} (deg)	30.05	30.01
data set (<i>h</i> ; <i>k</i> ; <i>l</i>)	-15 to +17; -17 to +17; -18 to +18	-10 to +10; -13 to +13; -32 to +32
total and unique no. of data; <i>R</i> (int)	16 075, 10 478; 0.0400	9244, 4980; 0.0214
no. of obsd data (<i>I</i> > 2σ(<i>I</i>))	6982	4177
no. of rflns, no. of params	10478, 420	4980, 216
<i>R</i> 1, <i>wR</i> 2, <i>G</i> OF	0.0921, 0.2492, 0.823	0.0330, 0.0959, 1.107

Crystal Structure Determinations. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) (Table 7). Data were collected using ψ scans, the structures were solved by direct methods using the SHELX97 software,^{56,57} and the refinement was by full-matrix least squares on *F*². No absorption correction was used. All non-hydrogen atoms were refined anisotropically, with H atoms introduced as fixed contributors (*d*_{C-H} = 0.95 Å, *U*₁₁ = 0.04). Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 618435 and 618436. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)-1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: CIF files giving crystallographic data for **13** and **17**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(56) Kappa CCD Operation Manual; Nonius BV: Delft, The Netherlands, 1997.

(57) Sheldrick, G. M. SHELXL97, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.