Notes

Activation of Polymerization Catalysts: Synthesis and Characterization of Novel Dinuclear Nickel(I) Diimine Complexes

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*Summary: The reaction of 1,4-bis(diisopropylphenyl)-aza-1,4-butadienenickel dibromide (**1a**) with stoichiometric amounts of phenyl Grignard or trimethylaluminum affords the purple Ni-(I) complexes **1b** and **1c**, respectively. Single-crystal X-ray diffraction reveals dinuclear species in the solid state for both compounds. UV/vis spectroscopy supports this rare oxidation state of nickel.*

With the work of Brookhart in the mid 1990s, late transition metal catalysts such as **1a** (Scheme 1) became available.[1] After activation, these catalysts produce branched products exclusively from ethylene.[2] This discovery caused considerable interest, as it opened the chance to generate high-value products from cheap monomer supplies.[3] However, the predominantly[4] used neutral dibromide complexes are rapidly and quantitatively deactivated in the presence of hydrogen, a reductant commonly used as a chain transfer reagent.[4d] The present contribution reports on the formation of neutral, dinuclear, and hydrogen-sensitive Ni(I) intermediates that are formed during the catalyst activation process.

Activation of the neutral dibromo (**1a**) or monocationic acetylacetonato species (**2a**,**b**) was performed by treatment with aluminum alkyls, such as trimethyl aluminum (TMA) or MAO, and was assumed to generate polymerization-active cationic Ni-(II) alkyl complexes.[5] Such compounds were characterized at −78 °C by NMR spectroscopy in previous studies.[6] Experiments with **1a** as catalyst precursor performed in our laboratories, however, revealed intense purple colors after treatment with aluminum alkyls, which is unusual for Ni(II) derivatives. In the 1970s tom Dieck reported on CH activation reactions of similar, *N*-isopropyl-substituted $NiBr_2$ complexes after reaction with *ortho*-CH_3-PhMgBr.[7] Later on, Brookhart observed a color change from dark blue α-diimine nickel(II) dipropyl solutions to purple while heating to room temperature.[4c] These results prompted us to react **1a** with phenyl Grignard (Ni/Mg = 1) to study the alkylation process. Indeed, immediately after Grignard addition to a brownish-orange diethyl ether suspension of **1a**, an intensive, deep purple color developed. An identical color change was observed by application of either TMA or MAO (Ni/Al = 1:3). Dark purple, temperature- and water-stable, but extremely oxygen-sensitive crystals were obtained from the Grignard (**1b**) and the TMA (**1c**) reaction. Both dinuclear Ni(I) complexes were isolated in up to 70% yield.[8] This rare nickel oxidation state was supported by UV/vis experiments performed on the deeply colored toluene solutions of **1b**,**c** (Table 1).[9]

One possible mechanism for the formation of such Ni(I) compounds comprises the dialkylation of a (α-diimine)Ni(II) complex. This initial step is followed by a rapid reductive elimination producing a Ni(0) intermediate that is stabilized in a comproportion reaction with remaining **1a**. A similar sequence

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

(2) (a) Gates, D. P.; Svejda, S. A.; Onate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320. (b) Brookhart, M.; Ittel, S. D.; Johnson, L. K. *Chem. Rev.* **2000**, *100*, 1169.

(3) In 2004 35 mio tons of PE-LD/PE-LLD and 25 mio tons of PE-HD were consumed worldwide, and consumption is estimated to grow by 5% p.a. at least until 2010. PlasticsEurope Deutschland, WG Statistics and Market Research; cf. http://www.vke.de/de/infomaterial/download/.

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(5) All attempts failed to achieve crystallizable $NiBr_2$ complexes of sterically bulky ligands, such as *N*,*N*′-bis(2,6-(4-*tert*-butylphenyl)phenyl)-1,4-diazabutadiene. Therefore, the monoanionic Ni(acac) complexes were applied. Moody, L. S.; Mackenzie, P. B.; Killian, C. M.; Lavoie, G. G.; Ponasik, J. A., Jr.; Barrett, A. G.; Smith, T. W.; Pearson, J. C. WO 00/50470, 2000.

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(7) tom Dieck, H.; Svoboda, M. *Chem. Ber.* **1976**, *109*, 1657−1664.

(8) Recently, investigations on monomeric anilido-imine Ni(I) complexes were published the following. (a) Wang, H.-Y.; Meng, X.; Jin, G.-X. *Dalton Trans.* **2006**, 2579 (b) Zhang, D.; Jin, G.-X.; Weng, L.-H.; Wang, F. *Organometallics* **2004**, *23* (13), 3270

(9) Due to the paramagnetic character of **1b**,**c** NMR experiments were unsuccessful.

10.1021/om060842s CCC: $37.00

Scheme 1. α-Diimine Nickel Complexes

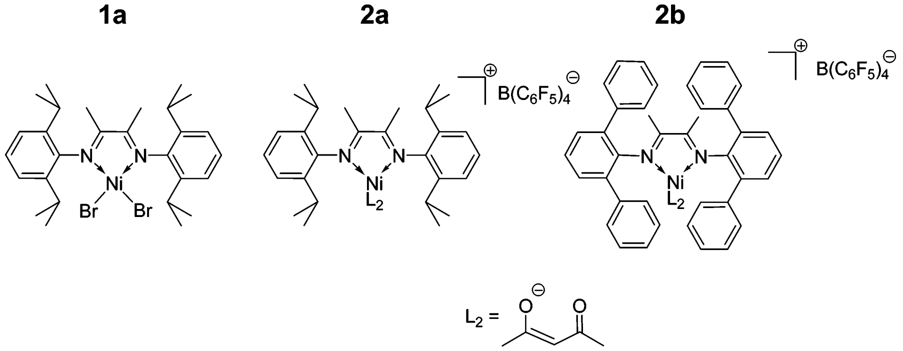

Table 1. Experimental UV/Vis Signals for 1b,c and the Polymerization-Inactive Species

	λ in nm (ϵ in L/(mol × cm))^a		
complex	λ_1^{b}	λ_2	λ_3
1b	300, 352sh	514sh, 556	**740(1321)**
1c	300, 348sh	502sh, 554	**750(1720)**
2a + H_2	308, 346sh	461sh, 495	**621(4260)**

^{a} Main maxima are bold. ^{b} The intensive UV band is solvent invariant and appears to be characteristic for the ligand.

Table 2. Crystal Data and Structure Refinement Parameters of 1b and 1c

	1b	1c
molecular composition	$C_{64}H_{96}Br_4MgN_4Ni_2O2$	$C_{56}H_{80}Br_2N_4Ni_2$
cryst syst	triclinic	triclinic
space group	*P*2(1)/*n*	*P*2(1)/*n*
a, Å	13.156(3)	13.714(3)
b, Å	16.357(3)	14.086(3)
c, Å	16.792(3)	14.814(3)
α, deg	90.00	90.00
β, deg	101.86	103.48(3)
γ, deg	90.00	90.00
vol, Å^3	3536.1(12)	2783.0(10)
mol wt	1414.82	1086.48
Z	2	2
ρ(calcd), g/cm^3	1.329	1.297
cryst size, mm^3	0.30 × 0.40 × 0.30	0.40 × 0.30 × 0.30
recrystallization solvent	diethyl ether	diethyl ether
refinement method	full-matrix least-squares on F^2	
radiation used μ, cm^{-1}	Mo Kα, 0.71073	Mo Kα, 0.71073
2θ range, deg	1.76−24.15	2.02−25.99
hkl range	$-15 \le h \le 15$	$-15 \le h \le 16$
$-18 \le k \le 18$	$-17 \le k \le 17$	
$-19 \le l \le 19$	$-18 \le l \le 18$	
no. of collected reflns	22 424	23 528
no. of unique reflns	5461	5287
no. of obsd reflns ($I > 2\sigma(I)$)	2779	3286
goodness-of-fit	0.755	0.880
final *R* incides ($I > 2\sigma(I)$)	R1 = 0.1088, wR2 = 0.0498	R1 = 0.0814, wR2 = 0.0418
R indices (all data)	R1 = 0.1303, wR2 = 0.1094	R1 = 0.0892, wR2 = 0.0804

was already described by tom Dieck[10] and finds further support by the fact that monocationic **2a**,**b** acac complexes do not give such dinuclear Ni(I) compounds. Due to the absence of stabilizing bromo ligands, treatment of **2a**,**b** with Al(III)-alkyl affords the precipitation of black Ni(0) (Scheme 2).

Suitable crystals of **1b**,**c** were submitted to X-ray diffraction analysis, which revealed the formation of dimeric Ni(I) species (Figure 1, Figure 2). Both unit cells include two Ni(I) dimers that possess a tetragonal coordination geometry.[11] In case of **1b**, the two Ni(I) fragments are stabilized by two μ^2-Br ligands (**1b**, Br1NiBr1* ≈ 94°, NiBr1 = 2.42 Å, and NiBr1* = 2.43 Å), whereas the application of the phenyl Grignard reagent affords a trinuclear, dimetallic complex (**1c**), consisting of two Ni(I)Br moieties, coordinated octahedrally to a Mg(II)Br_2(thf)$_2$ fragment (**1c**, Br1NiBr2 ≈ 97°, NiBr1 = 2.41 Å, and NiBr2 = 2.42 Å). In **1b** the Ni(I) atoms are bridged by the two μ^2-bromo ligands, affording a Ni−Ni distance of approximately 3.30 Å. The Ni−Ni diagonal in **1c** (7.09 Å) appears to be about twice as long, due to the $MgBr_2thf_2$ spacer unit.[10]

1b,**c** do not show any detectable polymerization activity toward monomers, such as ethylene, 1-hexene, and cyclic olefins (Scheme 2). Both Ni(I) complexes decomposed rapidly and quantitatively by contact with hydrogen to give black Ni(0).[12] If an excess of Al(III)-alkyl activator, however, is added, **1b**,**c** are converted into polymerization-active species again. We have no genuine explanation for this surprising effect, but speculate on a disproportion reaction of the Ni(I) dimers into Ni(0)[13] and polymerization-active (α-diimine)Ni(II) catalysts.

The above-described dinuclear Ni(I) compounds just form from dihalogeno-Ni complex precursors in the presence of low Al/Ni ratios. Therefore, they will most presumably not play a major role in solution polymerization experiments, which are mostly run at high Al/Ni ratio. However, this might change in experiments that apply supported catalysts for particle-forming reactions, because they use much lower Al loadings. It might well be that, especially in the presence of hydrogen, higher activities could be found, because Ni(I) decomposed readily under such conditions.

Experimental Section

Toluene and diethylether (Merck, p.a.) were purified by distillation over $LiAlH_4$ and dichloromethane by distillation over CaH_2. TMA and MAO were purchased as 2 M solutions in toluene from Crompton GmbH and Ni^{II}(acac)$_2$ from Merck. Ethylene (Linde, grade 3.0) and hydrogen (Linde, grade 5.0) were used as received. Trityltetrakis(pentafluorphenyl)borate[14] and **1a**[1] were prepared

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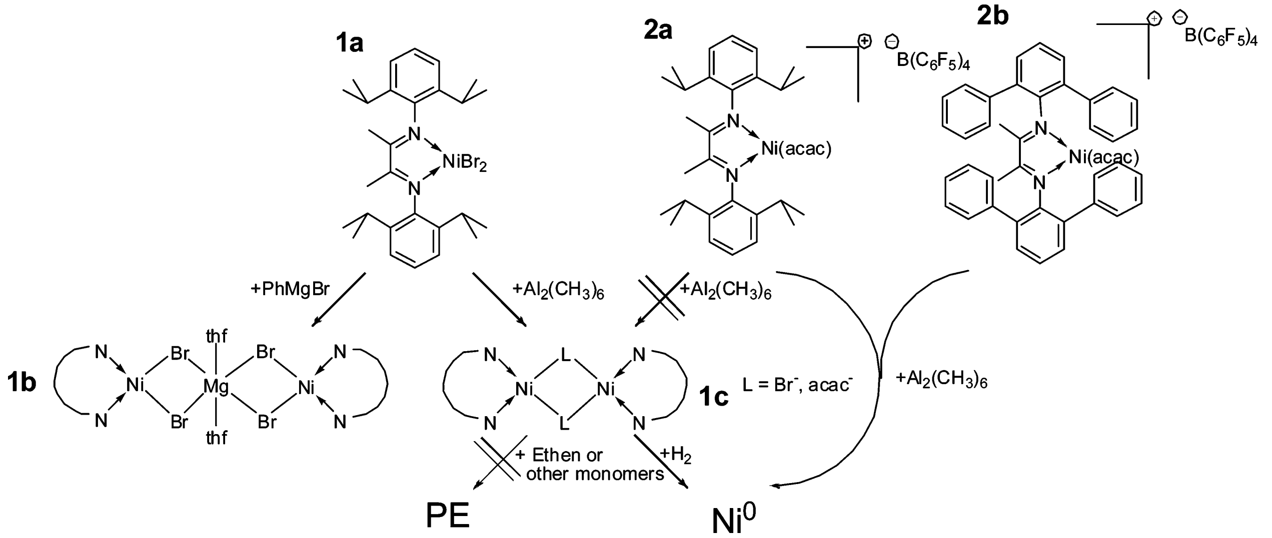
[10] tom Dieck, H.; Svoboda, M.; Kopf, J. *Z. Naturforsch. B: Chem. Sci.* **1978**, *33b*, 1381.

[11] Shao, Q.; Sun, H.; Shen, Q.; Zhang, Y. *Appl. Organomet. Chem.* **2004**, *18*, 289.

[12] Polymerization behavior of **1a** was published earlier; see ref 1. The experimental results for **2a**,**b** will be presented in future works.

[13] Treatment of **1a** and **2a** with TMA in solution afforded the rapid precipitation of Ni(0). We observed, however, dissolution of this black precipitate and a "blue, soluble but polymerization-inactive species" formed in the presence of Al(III) activators and ethylene monomer. All trials to grow crystals suitable for X-ray analysis of the blue compound remained unsuccessful until now. Therefore, we cannot give a structural suggestion yet. UV/vis spectroscopy points toward the formation of a Ni(II)-dialkyl species. For a similar observation of such a blue compound, see: Peruch, F.; Cramail, H.; Deffieux, A. *Macromolecules* **1999**, *32* (24), 7977−7983.

Scheme 2. Activation Pathways of 1a and 2a



according to published procedures. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Crystals were prepared in a glovebox (Braun).

We performed all polymerization reactions in a 250 mL double-walled jacketed flask connected to a external thermostat. Ethylene and hydrogen were continuously fed to the running reaction through calibrated liquid (Bronkhorst Liqui Flow Sensor L2) or gas flow meters (Bronkhorst F-201C) at constant pressure. Continuous hydrogen addition was performed by a master-slave control system that allows dosing a defined amount of H_2 with respect to ethylene consumption (Bronkhorst E-7000). The system was set up to obtain a constant mole fraction X [n mmol H_2/n mol C_2H_4] that corresponds to 0 to 75 mL of hydrogen per minute. UV/vis experiments were performed using a Specord 50 (AnalytikJena) spectrometer with a standard cuvette.

General Procedure for (ArN=C(CH$_3$)−C(CH$_3$)=NAr)Ni(acac)B(C$_6$F$_5$)$_4$ (1b, Ar = 2,6-C$_6$H$_3$(iPr)$_2$; 2b, Ar = 2,6-C$_6$H$_3$-(C$_6$H$_5$)$_2$). The corresponding α-diimine ligand (1.0 equiv) and Ni(acac)$_2$ (1.0 equiv) were dissolved in 15 mL of dry CH_2Cl_2. Trityltetrakis(pentafluorphenyl)borate (1.0 equiv) in 12 mL of dry CH_2Cl_2 was added slowly through a syringe. The resulting dark red solution was stirred over night and afterward filtered on an alumina column, using CH_2Cl_2 as eluent. The volume was reduced *in vacuo* to 15 mL, and *n*-pentane was added slowly to precipitate the complex. The lightly colored supernatant was removed, and the complex was taken up in 15 mL of CH_2Cl_2. The filtration procedure was repeated four times.

Analytical Data for 1b. α-Diimine (1.66 mmol, 0.671 g), Ni(acac)$_2$ (1.66 mmol, 0.427 g), and [CPh$_3$][B(C$_6$F$_5$)$_4$] (1.66 mmol, 1.533 g) were used. **1a** was obtained as a purple-red crystalline powder; yield 2.08 g (96%). ^{1}H NMR (δ = ppm, 400.13 MHz, $C_2D_2Cl_4$): δ 1.37 (d, 12H, CHCH$_3$), 1.46 (d, 12H, CHCH$_3$), 1.46 (s, 6H, CH$_3$), 1.60 (s, 6H, CH$_3$), 3.33 (sept, 4H, CHCH$_3$), 5.37 (s, 1H, CH), 7.27 (d, 4H$_{\rm arom}$), 7.47 (t, 2H$_{\rm arom}$). ^{13}C NMR (δ = ppm, 100.61 MHz, $C_2D_2Cl_4$): δ 20.19, 23.56, 23.88, 29.43, 102.37, 122.0−126.4 (br q, C−B), 124.65, 127.41, 127.99, 128.09, 130.36, 136.10, 136.26 (br d, $^1J_{\rm CF}$ = 238.58 Hz), 138.18 (br d, $^1J_{\rm CF}$ = 242.92 Hz), 140.77, 146.79, 148.14 (br d, $^1J_{\rm CF}$ = 233.51 Hz), 168.03, 187.59. MS (MALDI) *m*/*z*: 562.4 ([M$^+$ − borate], 100). Anal. Calcd for $C_{57}H_{47}BF_{20}N_2NiO_2$ (1241.5): C 55.15, H 3.82, N 4.73. Found: C 55.19, H 3.76, N 4.70.

Analytical Data for 2b. α-Diimine ligand (1.56 mmol, 0.84 g), Ni(acac)$_2$ (1.56 mmol, 0.40 g), and [C(C$_6$H$_5$)$_3$][B(C$_6$F$_5$)$_4$] (1.56 mmol, 1.44 g) were used. Complex **2b** was obtained as a dark red glassy powder; yield 2.04 g (95%). ^{1}H NMR (δ in ppm; 400.13 MHz, $C_2D_2Cl_4$): δ 1.44 (s, 6H, CH$_3$), 1.60 (s, 6H, CH$_3$), 5.34 (s, 1H, CH), 7.20−7.35 (m, 14H$_{\rm arom}$), 7.45−7.55 (m, 12H$_{\rm arom}$). ^{13}C NMR (δ in ppm; 100.61 MHz,$C_2D_2Cl_4$): δ 20.37, 24.35, 101.89, 122.5−125.5 (br q, C−B), 128.64, 128.77, 129.27,129.35, 130.94, 136.26 (br d, $^1J_{\rm CF}$ = 250.29 Hz), 136.28, 136.59, 138.18 (br d, $^1J_{\rm CF}$ = 248.09 Hz), 138.69, 148.18 (br d, $^1J_{\rm CF}$ = 240.00 Hz), 176.17, 186.48. MS (MALDI) *m*/*z*: 697.4 ([M$^+$ − borate], 100).

Synthesis of (ArN=C(CH$_3$)−C(CH$_3$)=NAr)NiBr)$_2$MgBr$_2$thf$_2$ (1b) (Ar = 2,6-C$_6$H$_3$(iPr)$_2$). The α-diimine Ni(II) complex **1a** (630 mg, 1 mmol) was suspended in Et$_2$O (20 mL). The reaction was cooled to −15 °C. The phenyl Grignard reagent (Merck), diluted in Et$_2$O (15 mL), was added slowly. The suspension changed color

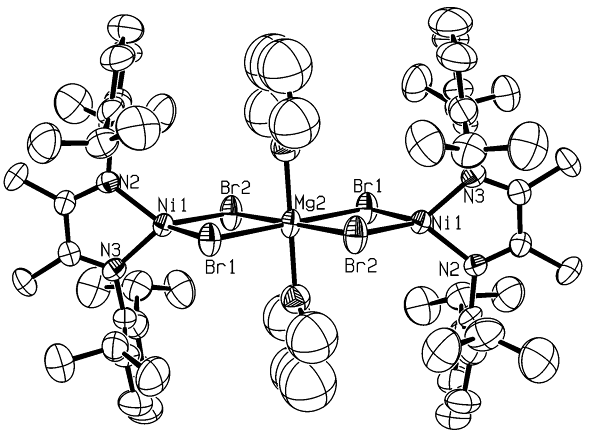


Figure 1. ORTEP-imaged complex **1b**. The atoms are drawn as 50% thermal ellipsoids. H atoms are excluded for clarity.

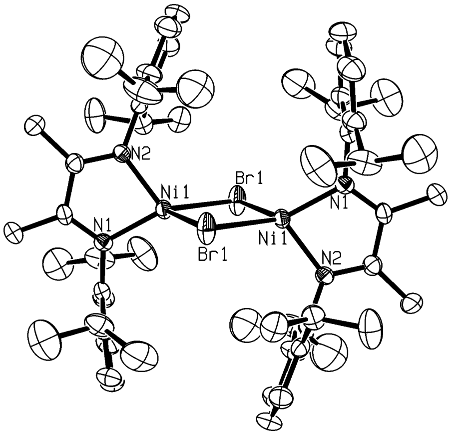


Figure 2. ORTEP-imaged complex **1c**. The atoms are drawn as 50% thermal ellipsoids. H atoms are excluded for clarity.

spontaneously from orange to dark violet. After complete addition the solution was stirred further for 30 min. The organic phase was washed with water (20 mL). After separation the aqueous phase was extracted with Et_2O (5 mL). The combined organic phases were evaporated *in vacuo* to give 990 mg of **1b** (70% of theory). Crystals of **1b** suitable for X-ray diffraction analysis were obtained by recrystallization in Et_2O.

Synthesis of $(ArN{=}C(CH_3){-}C(CH_3){=}NAr)_2Ni_2Br_2$ (1c) (Ar = 2,6-$C_6H_3(iPr)_2$). The α-diimine Ni(II) complex **1a** (630 mg, 1 mmol) was suspended in Et_2O (20 mL). The reaction was cooled to −78 °C. Then the TMA toluene solution (1.5 mL of a 2 M solution), diluted in Et_2O (15 mL), was added slowly (30 min) to the solution. After complete addition, the reaction was brought to room temperature and stirred for 2 h. The organic phase was washed with water (20 mL). After separation the aqueous phase was extracted with Et_2O (5 mL). The combined organic phases were evaporated to dryness to give 706 mg of **1c** (65% of theory). Crystals of **1c** suitable for X-ray diffraction were obtained by recrystallization from the corresponding ether solution.

CCDC 627203 and 627204 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: Crystallographic information files (CIFs). This material is available free of charge via the Internet at http://pups.acs.org.

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