Activation of chlorobenzene with Ni(0) *N*,*N*-chelates — A remarkably profound effect of a minuscule change in ligand structure[1]

William J. Marshall and Vladimir V. Grushin

Abstract: Activation of the C—Cl bond of chlorbenzene with [(COD)$_2$Ni] and a bidentate *N*,*N*-ligand such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) and 2,2′-bipyridyl (bipy) has been reported to produce σ-phenyl complexes [(tmeda)Ni(Ph)Cl] (**1**) and [(bipy)Ni(Ph)Cl], respectively. However, in sharp contrast, we found that similar reactions involving almost the identical ligands *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (teeda) and 6,6′-dimethyl-2,2′-bipyridyl (6,6′-Me$_2$bipy) resulted in homocoupling and the formation of non-organometallic dichlorocomplexes [(teeda)NiCl$_2$] and [(6,6′-Me$_2$bipy)NiCl$_2$]. The latter two compounds and **1** were characterized by single-crystal X-ray diffraction data. The remarkable change in the reaction outcome points to its extremely high sensitivity to minor alterations in the structure of the stabilizing *N*,*N*-ligand. In contrast, analogous reactions of [Pd(dba)$_2$] with PhI in the presence of teeda or 1,2-dipiperidinoethane (dpe) produced the expected σ-phenyl complexes [(teeda)Pd(Ph)I] and [(dpe)Pd(Ph)I], much like the previously reported reaction with tmeda.

Key words: C-Cl activation, zerovalent nickel complexes, *N*,*N*-ligands, oxidative addition, homocoupling, X-ray analysis.

Résumé : Il a été rapporté antérieurement que l'activation de la liaison C—Cl du chlorobenzène à l'aide de [(COD)$_2$Ni] et d'un ligand *N*,*N* bidentate, tel la *N*,*N*,*N*′,*N*′-tétraméthyléthylènediamine (tmeda) ou le 2,2′-bipyridyle (bipy), conduit à la formation de complexes σ-phényles, tels le [(tmeda)Ni(Ph)Cl] (**1**) et le [(bipy)Ni(Ph)Cl] respectivement. Les observations faites dans ce travail contrastent fortement avec ces résultats alors que des réactions semblables impliquant les ligands très semblables *N*,*N*,*N*′,*N*′-tétraéthyléthylènediamine (teeda) et 6,6′-diméthyl-2,2′-bipyridyle (6,6′-Me$_2$bipy) conduisent à un homocouplage et à la formation des dichlorocomplexes non-organométalliques [(teeda)NiCl$_2$] et [(6,6′-Me$_2$bipy)NiCl$_2$]. Ces deux derniers complexes et le composé **1** ont été examinés par diffraction des rayons X sur un cristal unique. Les changements remarquables observés dans les résultats de ces réactions indiquent qu'ils sont extrêmement sensibles à des changements mineurs dans la structure du ligand *N*,*N* stabilisateur. Au contraire, les réactions analogues du [Pd(dba)$_2$] avec le PhI en présence de teeda ou de 1,2-dipipéridinoéthane (dpe) ont conduit aux complexes σ-phényles attendus [(teeda)Pd(Ph)I] et [(dpe)Pd(Ph)I], tel qu'il avait été observé antérieurement dans les réactions avec le tmeda.

Mots clés : activation de la liaison C-Cl, complexes zérovalent du nickel, ligands *N*,*N*, addition oxydante, homocouplage, analyse de diffraction des rayons X.

[Traduit par la Rédaction]

Introduction

Catalysis with metal complexes is the primary tool for solving the problem of the notoriously low reactivity of non-activated (1, 2) haloarenes toward nucleophiles. Considerable progress (3–16) has been made in the development of catalytic transformations of aryl halides and triflates, Ar–X (X = Cl, Br, I, OTf), such as Kumada, Suzuki–Miyaura (11), and Negishi (12) coupling, the Mizoroki–Heck olefin arylation (13), and various carbonylation, amination (14, 15), and cyanation (16) reactions. Palladium tertiary phosphine complexes are most often used as catalysts for these reactions. Some bidentate nitrogen (17) and *N*-heterocyclic carbene (18–21) ligands have recently been offered as an alternative to organic phosphines for Pd catalysis. While in general tertiary amines are poorly efficient stabilizing ligands in Pd catalysis, the recently reported Pd(OAc)$_2$–Dabco catalytic system demonstrates high efficiency in Suzuki–Miyaura coupling (22).

Nickel, a metal that is considerably less costly than palladium, is also often used for cross-coupling reactions of haloarenes. The Ar—X bond is activated by Ni(0) more easily than by Pd(0), as illustrated by the chemistry of poorly

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Dedicated to Professor Howard Alper.

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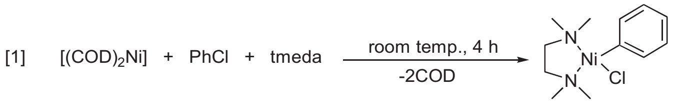
reactive chloroarenes (6, 23). However, oxidative addition of the Ar—X bond to Ni(0), the first key step of the catalytic loop, is often complicated, especially for X = I and Br, by radical processes (6, 24, 25) and homocoupling, also known as the Semmelhack reaction (8, 26, 27). We were interested in the oxidative addition of chloroarenes to Ni(0) stabilized with diamine ligands, to explore the possibility of using such systems as catalysts for carbon–heteroatom bond formation.

Results and discussion

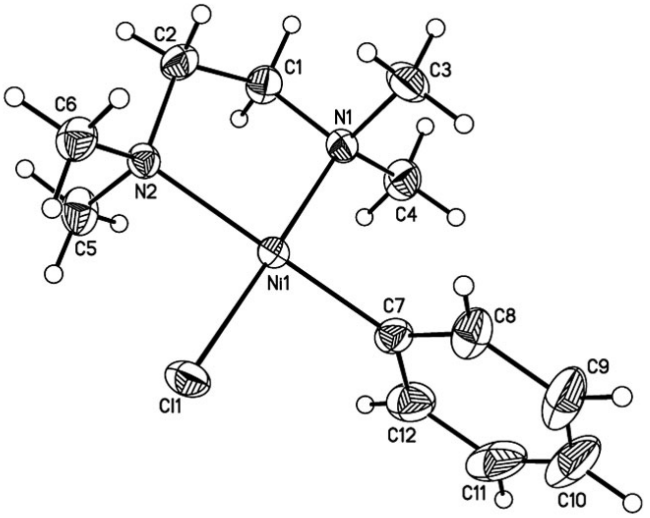
In 1987, Wenschuh and Zimmering (28) reported the formation of [(tmeda)Ni(Ph)Cl] (**1**) (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) in 76% isolated yield upon oxidative addition of PhCl to [$(COD)_2Ni$] (COD = 1,5-cyclooctadiene) in the presence of tmeda at room temperature (eq. [1]).



1, 76%

No characterization of **1** was presented in the article (28), although SO_2 insertion into the Ni—C bond was later reported by the same group (29). Having prepared orange-yellow **1** in 70%–89% yield via the Wenschuh–Zimmering procedure, we attempted characterization of this complex. The composition of **1** was confirmed by satisfactory C, H, N microanalysis data. It was found that **1** is insoluble in alkanes, benzene, toluene, and ether, and slightly soluble in THF (28). Although **1** is easily soluble in CH_2Cl_2 and 1,2-dichloroethane (dce), these chlorinated solvents decompose **1** even at room temperature within a few minutes (CH_2Cl_2) or several hours (dce). We succeeded in obtaining ^1H and ^{13}C NMR data for **1** in dce-d_4. At room temperature, the ^1H NMR spectrum of **1** exhibited three sharp aromatic resonances at 6.6 (1H, *p*-Ph), 6.7 (2H, *m*-Ph), and 7.5 (2H, *o*-Ph) ppm along with a broadened multiplet at 2.0–2.7 ppm from the aliphatic protons. The ^{13}C NMR spectrum recorded at 20 °C displayed two signals from the methyl groups (47.1 and 49.3 ppm), two methylene resonances (56.9 and 61.1 ppm), and four aromatic peaks (121.4, 124.5, 136.8, and 147.5 ppm). The aromatic lines were sharp, whereas considerable line broadening ($\Delta\nu_{1/2}$ = 15–20 Hz) was observed for the methyl and methylene resonances. The latter sharpened to $\Delta\nu_{1/2}$ = 10 Hz upon cooling to 10 °C, indicating that some exchange processes were occurring. Although studying these dynamic processes was beyond the scope of our work, the ambient temperature NMR spectra were fully consistent with the structural formula of **1** as shown in eq. [1].

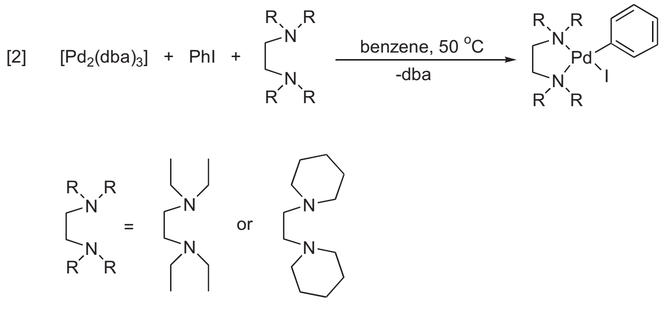
Fig. 1. An ORTEP drawing of **1** with thermal ellipsoids drawn to the 50% probability level. Selected bond distances (Å) and angles (°): Ni(1)—C(7) 1.891(2), Ni(1)—N(1) 1.971(1), Ni(1)—N(2) 2.053(1), Ni(1)—Cl(1) 2.184(1); C(7)-Ni(1)-N(1) 92.61(6), C(7)-Ni(1)-N(2) 179.33(6), N(1)-Ni(1)-N(2) 86.72(5), C(7)-Ni(1)-Cl(1) 88.49(5), N(1)-Ni(1)-Cl(1) 178.80(4), N(2)-Ni(1)-Cl(1) 92.17(3).



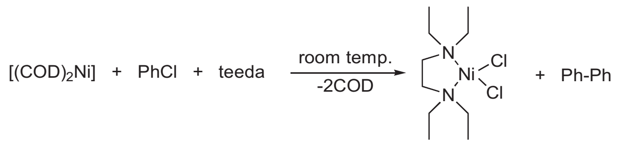
X-ray quality crystals of **1** were obtained from dce–hexanes. Two polymorphic crystalline forms of **1** were observed, thin needles (major) and irregular blocks (minor). Both forms were analyzed by X-ray diffraction. The structure of **1** determined for the thin needle polymorph (*C*2/*c*, *a* = 22.96(2) Å, *b* = 7.828(8) Å, *c* = 16.56(1) Å, β = 115.04(4)°) was of poor quality due to its small crystal size. A good quality X-ray structure of **1** (Fig. 1) was obtained for one of the irregular block crystallites. The molecule of **1** is square-planar, as expected from a diamagnetic (see the NMR data above) Ni(II) complex. In accord with trans-influence considerations, the Ni—N bond trans to Ph (2.053(1) Å) is longer than that trans to Cl (1.971(1) Å). The aromatic ring is orthogonal to the coordination plane of the complex, as in the closely related structure [(tmeda)Pd(Ph)I] (30).

The aforementioned decomposition of **1** in chlorinated solvents was found to produce pale green crystals, which we identified by X-ray analysis as [$(tmeda)_3Ni_3(\mu\text{-}Cl)_3(\mu^3\text{-}Cl)(\mu^3\text{-}OH)]^+Cl^-$ whose X-ray structure has been reported previously (31, 32). Because **1** was handled under rigorously anhydrous conditions, the source of OH for the trinuclear complex was probably the surface of the glass.

Although the structure of **1** was established, the complex was of limited further use for stoichiometric and catalytic studies because of its poor solubility. It was then reasoned that the teeda analogue of **1** ([(teeda)Ni(Ph)Cl], teeda = *N*,*N*,*N*′,*N*′-tetraethylethylenediamnie), should be more readily soluble in organic solvents and hence suitable for further studies. Indeed, the closely related Pd complexes [(teeda)Pd(Ph)I] and [(dpe)Pd(Ph)I] (dpe = 1,2-dipiperidinoethane) were prepared (eq. [2]) by the procedure reported (30) for [(tmeda)Pd(Ph)I] and were found to be more soluble than the latter.



Surprisingly, however, the reaction of [(COD)$_2$Ni] with PhCl in the presence of teeda did not afford [(teeda)Ni(Ph)Cl], but rather Semmelhack-type coupling occurred to produce deep-purple, paramagnetic [(teeda)NiCl$_2$] (eq. [3]).

[3]


The structure of the complex [(teeda)NiCl$_2$] was established by X-ray analysis, showing tetrahedral coordination geometry around Ni (Fig. 2). In accord with the tetrahedral structure, two broad lines at 7.5 and 11.9 ppm were observed in the ^{1}H NMR spectrum of paramagnetic [(teeda)NiCl$_2$] in benzene-d_6.

Considering the minor change in the structures of tmeda and teeda, the difference in the outcomes of the two reactions (eqs. [1] and [3]) is remarkable. The tmeda vs. teeda case, however, is not unique. While it has been reported (28) that the reaction of [(COD)$_2$Ni] with 2,2′-bipyridyl (bipy) and PhCl leads to a nickel aryl ([(bipy)Ni(Ph)Cl]), we found that 6,6′-dimethyl-2,2′-bipyridyl (6,6′-Me$_2$bipy) produces the paramagnetic inorganic dichloride [(6,6′-Me$_2$bipy)NiCl$_2$] under similar conditions (eq. [4] and Fig. 3). No *N*-chelated Ni complexes were formed when [(COD)$_2$Ni] was reacted with PhCl and *N,N,N′,N′*-tetraisopropylethylenediamine (tipeda). Considering the well-known low nucleophilicity of sterically hindered Hunig's base (i-Pr$_2$NEt), this observation is not surprising. Nonetheless, a simple high-yield preparation of tipeda is presented in the Experimental section.

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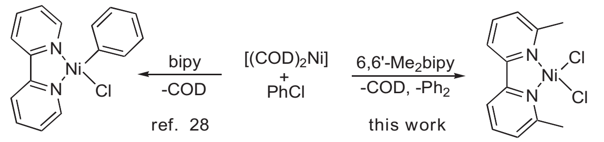


Fig. 2. An ORTEP drawing of [(teeda)NiCl$_2$] with thermal ellipsoids drawn to the 50% probability level. Selected bond distances (Å) and angles (°): Ni(1)—N(1) 2.050(2), Ni(1)—N(2) 2.059(2), Ni(1)—Cl(1) 2.232(1), Ni(1)—Cl(2) 2.232(1); N(1)-Ni(1)-N(2) 89.32(6), N(1)-Ni(1)-Cl(1) 107.12(4), N(2)-Ni(1)-Cl(1) 110.87(5), N(1)-Ni(1)-Cl(2) 110.60(5), N(2)-Ni(1)-Cl(2) 106.14(4), Cl(1)-Ni(1)-Cl(2) 126.50(2).

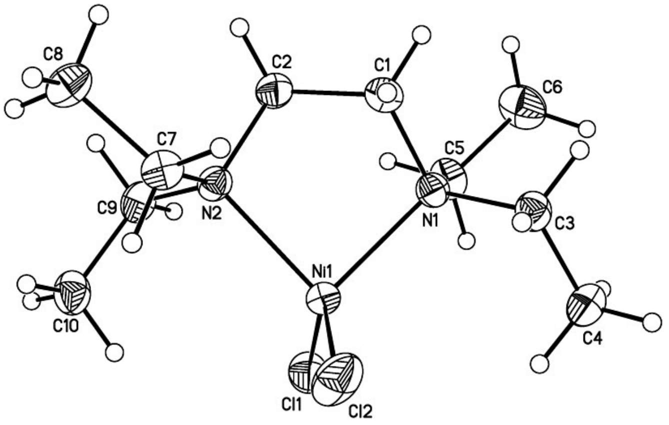
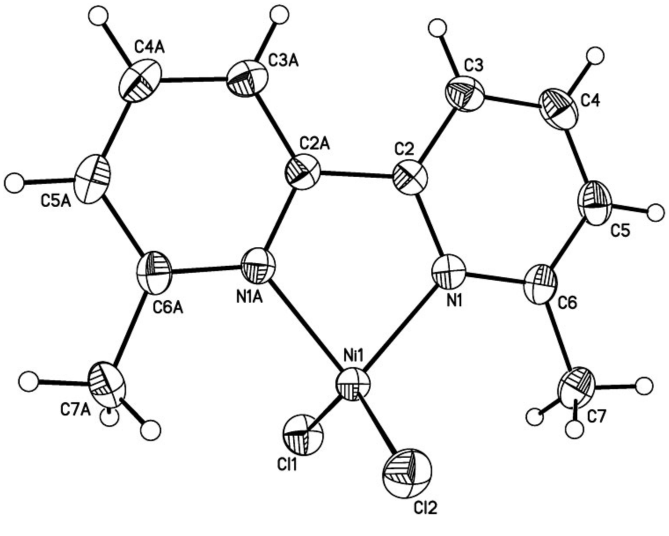


Fig. 3. An ORTEP drawing of [(6,6′-Me$_2$bipy)NiCl$_2$] with thermal ellipsoids drawn to the 50% probability level. Selected bond distances (Å) and angles (°): Ni(1)—N(1) 1.985(1), Ni(1)—N(1A) 1.985(1), Ni(1)—Cl(2) 2.211(1), Ni(1)—Cl(1) 2.218(1); N(1)-Ni(1)-N(1A) 82.76(7), N(1)-Ni(1)-Cl(2) 109.05(4), N(1A)-Ni(1)-Cl(2) 109.05(4), N(1)-Ni(1)-Cl(1) 105.80(4), N(1A)-Ni(1)-Cl(1) 105.81(4), Cl(2)-Ni(1)-Cl(1) 132.93(3).



At this point, it is unclear if the change in the reaction paths when going from tmeda to teeda or from bipy to 6,6′-Me$_2$bipy is largely due to electronic or steric (33) factors, or a combination of both. While considerable progress has been made in understanding the mechanisms of Semmelhack homocoupling of aryl halides (25, 27, 34), the results reported by different groups are not completely without controversy (34). The first step of the process is oxidative addition of Ar–X to Ni(0) to produce an aryl Ni(II) halide complex. Since chloroarenes are known to be almost unreactive toward [(COD)$_2$Ni] (26), a bidentate *N*-ligand should displace at least one COD in [(COD)$_2$Ni] before oxidative addition of PhCl can occur. As described by Tsou and Kochi (25) and discussed, most recently, in detail in an excellent review by Nelson and Crouch (34), an intermediate Ni(III) aryl species might play a key role in the homocoupling reaction. Aryl transfer from Ar–Ni(III) to Ar–Ni(II), possibly via a bridging intermediate, would produce a diaryl Ni(III) species that leads to biaryl upon C–C reductive elimination. Such Ar–Ni(III) species are more likely to emerge when more electron-rich teeda (vs. tmeda) and 6,6′-Me$_2$bipy (vs. bipy) are employed. On the other hand, one may not rule out the solubility factor, i.e., it is conceivable that the poorly soluble tmeda derivative **1** precipitates out immediately upon formation, whereas its more soluble teeda analogue may undergo further transformations in solution.

In conclusion, we have demonstrated that Ph–Cl activation by Ni(0) stabilized with *N*-chelating ligands does not necessarily form a σ-phenyl Ni species as the final product, but can also result in homocoupling and formation of the corresponding dichloro complex. The outcome of such reactions is remarkably sensitive to even small changes in the structure of the stabilizing *N*,*N*-ligand, as illustrated by the differing behavior of the tmeda and teeda systems. These observations might be important for the design of reactions of haloarenes, catalyzed by Ni *N*,*N*-chelate complexes.

Experimental

Materials and instruments

All manipulations with Ni complexes were conducted in a glovebox under N_2. All chemicals were purchased from Aldrich, Acros Organics, and Strem Chemical Companies. The diamines were distilled from CaH_2 under N_2 prior to use. Both [$(COD)_2Ni$] and 6,6′-Me_2bipy were used as received. All solvents were purified and (or) dried by standard techniques and stored over freshly activated molecular sieves (4 Å) in the glovebox. NMR spectra were obtained with Bruker Avance DPX 300 and DRX 400 instruments. A Bruker Smart 1 K CCD system was used for single crystal X-ray diffraction studies. Microanalyses were performed by Micro-Analysis, Inc., Wilmington, Delaware, USA.

Synthesis of [(tmeda)Ni(Ph)Cl] (1)

A slight modification of the reported procedure (28) was used. A solution of tmeda (0.28 mL) in chlorobenzene (2 mL) was added to [$(COD)_2Ni$] (0.42 g), and the mixture was stirred at room temperature for 6 h. Hexanes (10 mL) were added and the mixture was left at room temperature overnight. The orange-yellow precipitate was separated by filtration, thoroughly washed with hexanes, and dried under vacuum. The yield of **1** was 0.39 g (89%). ^1H NMR (1,2-dichloroethane-d_4, 20 °C) δ: 2.0–2.7 (m, 16H, CH_3 and CH_2), 6.6 (1H, *p*-Ph), 6.7 (2H, *m*-Ph), 7.5 (2H, *o*-Ph). ^{13}C NMR (1,2-dichloroethane-d_4, 20 °C) δ: 47.1 (br), 49.3 (br), 56.9 (br), 61.1 (br), 121.4, 124.5, 136.8, 147.5. Anal. calcd. for $C_{12}H_{21}ClN_2Ni$ (%): C 50.1, H 7.4, N 9.7; found: C 49.9, H 7.0, N 9.7.

Preparation of [(teeda)Pd(Ph)I]

Under N_2, a stirring mixture of $Pd(dba)_2$ (1.00 g), teeda (0.39 g), iodobenzene (0.51 g), and benzene (25 mL) was slowly heated to 50 °C and kept at that temperature for 15 min. The greenish reaction mixture was filtered through Celite®, which was then washed with benzene (2 × 10 mL). After the combined filtrate and washings were evaporated, the residue was washed with ether (3 × 10 mL) to remove dba. Recrystallization of the orange residue from dichloromethane–ether produced 0.30 g (36%) of [(teeda)Pd(Ph)I] as a pale yellow crystalline solid. ^1H NMR (dichloromethane-d_2, 20 °C) δ: 1.4 (t, *J* = 7.1 Hz, 6H, CH_3), 1.5 (t, *J* = 7.1 Hz, 6H, CH_3), 2.7 (m, 6H, CH_2), 2.8 (m, 2H, CH_2), 3.0 (m, 2H, CH_2), 3.2 (m, 2H, CH_2), 6.7 (m, 1H, *p*-Ph), 6.9 (m, 2H, *m*-Ph), 7.3 (m, 2H, *o*-Ph). Anal. calcd. for $C_{16}H_{29}IN_2Pd$ (%): C 39.8, H 6.0, N 5.8; found: C 39.7, H 6.0, N 5.7.

Preparation of [(dpe)Pd(Ph)I]

Under N_2, a stirring mixture of $Pd(dba)_2$ (1.00 g), dpe (0.44 g), iodobenzene (0.51 g), and benzene (25 mL) was slowly heated to 50 °C and kept at that temperature for 15 min. The greenish reaction mixture was filtered through Celite®, which was then washed with benzene (2 × 10 mL). After the combined filtrate and washings were evaporated, the residue was washed with ether (3 × 10 mL) to remove dba. Recrystallization of the residue from dichloromethane–ether produced 0.40 g (46%) of [(dpe)Pd(Ph)I] as "copper" orange flakes. ^1H NMR (dichloromethane-d_2, 20 °C) δ: 1.0–1.8 (m, CH_2), 2.7–3.1 (m, CH_2), 3.8 (m, CH_2), 6.8 (m, 1H, *p*-Ph), 6.9 (m, 2H, *m*-Ph), 7.3 (m, 2H, *o*-Ph). Anal. calcd. for $C_{18}H_{29}IN_2Pd$ (%): C 42.7, H 5.8, N 5.5; found: C 42.3, H 5.7, N 5.4.

Preparation of [(teeda)$NiCl_2$]

A solution of teeda (1.00 g) in chlorobenzene (2 mL) was added to [$(COD)_2Ni$] (1.22 g), and the mixture was stirred at room temperature overnight. Hexanes (8 mL) were added. After 30 min, the deep-purple solid was separated by filtration, washed with hexanes (4 × 10 mL), and dried under vacuum. The yield was 0.89 g (66%). Anal. calcd. for $C_{10}H_{24}Cl_2N_2Ni$ (%): C 39.8, H 8.0, N 9.3; found: C 39.8, H 7.3, N 9.2. X-ray quality crystals were grown from dichloromethane–hexanes.

Preparation of [(6,6′-Me_2bipy)$NiCl_2$]

A mixture of 6,6′-Me_2bipy (0.50 g), [$(COD)_2Ni$] (0.70 g), and chlorobenzene (6 mL) was stirred at room temperature for 1 day. A green color emerged immediately upon mixing the reagents, which then turned dark-blue within seconds, and finally light-purple. The light-purple solid was separated by filtration, washed with chlorobenzene (2 × 2 mL) and hexanes (2 × 3 mL), and dried under vacuum. The yield was 0.79 g (99%). Anal. calcd. for $C_{12}H_{12}Cl_2N_2Ni$ (%): C 45.9, H 3.8, N 8.9; found: C 46.0, H 3.7, N 8.7. X-ray quality crystals were grown from hot 1,2-dichloroethane.

Synthesis of *N*,*N*,*N′*,*N′*-tetraisopropylethylenediamine (tipeda)

In air, a mixture of 2-iodopropane (20 mL), ethylenediamine (1.1 mL), and potassium carbonate (9.2 g) was stirred under reflux for 58 h. The tan liquid phase was separated from the solids, which were then thoroughly washed with ether (10 × 5 mL). The mother liquor and the washings were combined, evaporated, and the residue distilled under vacuum (86–98 °C at 9.5 mm Hg, (1 mm Hg = 133.322 4 Pa) to produce 3.32 g (87%) of spectroscopically pure tipeda. ^1H NMR (benzene-d_6, 20 °C) δ: 1.1 (t, *J* = 6.6 Hz, 24H, CH_3), 2.7 (s, 4H, CH_2), 3.1 (heptet, *J* = 6.6 Hz, 4H, CH). ^{13}C NMR (benzene-d_6, 20 °C) δ: 21.4, 48.1, 49.4.

Crystallographic studies

All crystallographic data were collected using a Bruker Smart 1 K CCD system equipped with Mo Kα radiation at –100 °C. The structures were solved using direct methods and refined with the SHELXTL program suite (35). Scattering factors were obtained from the *International Tables for X-ray Crystallography* (36). Additional data and refinement

Table 1. Crystallographic data for [(tmeda)Ni(Ph)Cl] (**1**), [(teeda)NiCl$_2$], and [(6,6′-Me$_2$bipy)NiCl$_2$].

	[(tmeda)Ni(Ph)Cl] (**1**)	[(teeda)NiCl$_2$]	[(6,6′-Me$_2$bipy)NiCl$_2$]
Empirical formula	$C_{12}H_{21}ClN_2Ni$	$C_{10}H_{24}Cl_2N_2Ni$	$C_{12}H_{12}Cl_2N_2Ni$
FW	287.47	301.92	313.85
Crystal color, form	Gold, plate	Purple, irreg. block	Red-orange, irreg. block
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	*P*2(1)/*c*	*Pna*2(1)	*Pnma*
Unit cell dimensions			
a (Å)	11.0284(4)	14.7179(14)	14.594(2)
b (Å)	12.2967(5)	12.3740(12)	11.1805(15)
c (Å)	11.4778(4)	7.7454(7)	7.8560(11)
α (°)	90	90	90
β (°)	118.629(1)	90	90
γ (°)	90	90	90
V (Å^3)	1 366.24(9)	1 410.6(2)	1 281.9(3)
Z	4	4	4
Density (g cm^{-3})	1.398	1.422	1.626
Abs. μ (mm^{-1})	1.592	1.728	1.907
F(000)	608	640	640
Crystal size (mm^3)	0.22 × 0.08 × 0.04	0.45 × 0.42 × 0.24	0.35 × 0.35 × 0.32
Temp (°C)	–100	–100	–100
Scan mode	ω	ω	ω
Detector	Bruker CCD	Bruker CCD	Bruker CCD
θ_{max} (°)	28.3	28.26	28.29
No. obsrvd. reflections	10 437	7 106	10 052
No. uniq. reflections	3 392	2 146	1 589
R_{merge}	0.0251	0.0173	0.0258
No. of parameters	149	141	83
S^a	0.989	1.071	1.003
R indices [$I > 2\sigma(I)$]^b	$wR_2 = 0.0590$, $R_1 = 0.0244$	$wR_2 = 0.0446$, $R_1 = 0.0178$	$wR_2 = 0.0639$, $R_1 = 0.0238$
R indices (all data)^b	$wR_2 = 0.0618$, $R_1 = 0.0330$	$wR_2 = 0.0456$, $R_1 = 0.0189$	$wR_2 = 0.0664$, $R_1 = 0.0272$
Max diff. peak, hole (e Å^{-3})	0.358, –0.236	0.201, –0.239	0.383, –0.240

[a] GoF = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of refined parameters.

[b] $R_1 = \sum(|F_o| - |F_c|)/\sum |F_o|$, $wR_2 = \{\sum w(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$ (sometimes denoted as R_w2).

details are presented in Table 1. The crystal structures have been deposited as supplementary material.[4]

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[4] Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 3677. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 251780 (**1**), 251779 ([(teeda)NiCl$_2$)], and 251778 ([(6,6′-Me$_2$bipy)NiCl$_2$]) contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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