

# Direct Observation of $\beta$ -Chloride Elimination from an Isolable $\beta$ -Chloroalkyl Complex of Square-Planar Nickel

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**S** Supporting Information

**ABSTRACT:** Reported here are the isolation, structural characterization, and decomposition kinetics of the four-coordinate pentachloroethyl nickel complex,  $\text{NiCl}(\text{CCl}_2\text{CCl}_3)(\text{CNAr}^{\text{Mes}2})_2$  ( $\text{Ar}^{\text{Mes}2} = 2,6-(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$ ). This complex is a unique example of a kinetically persistent  $\beta$ -chloroalkyl in a system relevant to coordination–insertion polymerization of polar olefins. Kinetic analysis of  $\text{NiCl}(\text{CCl}_2\text{CCl}_3)(\text{CNAr}^{\text{Mes}2})_2$  decomposition indicates that  $\beta$ -chloride ( $\beta$ -Cl) elimination proceeds by a unimolecular mechanism that does not require initial dissociation of a  $\text{CNAr}^{\text{Mes}2}$  ligand. The results suggest that a direct  $\beta$ -Cl elimination pathway is available to four-coordinate, Group 10 metal vinyl chloride polymerization systems.

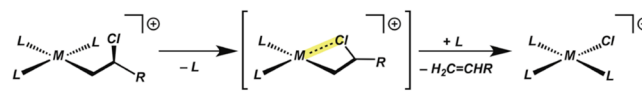
Investigations into the formation and decomposition of  $\beta$ -chloroalkyl ligands have been central to the ongoing quest for a coordination–insertion polymerization process for vinyl chlorides.<sup>1–3</sup> It is now well established that  $\beta$ -chloroalkyl ligands are susceptible to rapid and irreversible  $\beta$ -chloride ( $\beta$ -Cl) elimination and that this mode of decomposition deactivates a potential single-site polymerization catalyst toward subsequent insertion of other vinyl chloride or olefin monomers.<sup>4–6</sup> The origin of facile  $\beta$ -Cl elimination from  $\beta$ -chloroalkyl ligands has been traced to the differences between metal–carbon and metal–chlorine bond strengths.<sup>7</sup> For Lewis acidic early transition metals, formation of a strong M–Cl linkage with attendant  $\pi$ -donor interactions provides a substantial driving force for facile  $\beta$ -Cl elimination.<sup>4,5,8,9</sup> In late transition metal polymerization systems, where the M–C and M–Cl bond strengths are less disparate,<sup>10–12</sup> the driving force for  $\beta$ -Cl elimination from  $\beta$ -chloroalkyl ligands can be attenuated relative to early metal systems.<sup>13</sup>

While no efficient polymerization system has been identified in which  $\beta$ -Cl elimination is completely inhibited, several strategies aiming to overcome this challenge have been reported. These efforts have centered on the use of four-coordinate, Group 10 metal centers and ligand frameworks that seek to destabilize the transition state for  $\beta$ -Cl elimination<sup>3</sup> or accelerate olefin binding/insertion to a coordinatively unsaturated  $\beta$ -chloroalkyl complex.<sup>2,3,13,14</sup> More recently, efforts have focused on systems that encourage rapid 2,1-addition of vinyl chloride into a Group 10 metal–alkyl bond and low rates of subsequent  $\beta$ -H elimination/

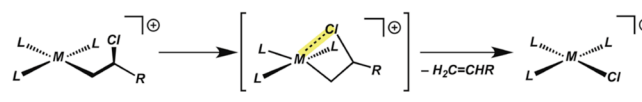
reinsertion (i.e., chain walking) to obviate the formation of a  $\beta$ -chloroalkyl ligand.<sup>15–17</sup> In the mechanistic scenarios guiding these studies, it is assumed that *syn*- $\beta$ -Cl elimination proceeds to an open coordination site within the basal plane of a nominally  $14e^-$ , T-shaped coordinatively unsaturated  $\beta$ -chloroalkyl complex (Scheme 1, Path A).<sup>2,13,15</sup> This pathway has been suggested

## Scheme 1. Generalized Mechanisms for $\beta$ -Cl Elimination in Square-Planar Group 10 Metal Complexes with and without Ligand Dissociation

### Path A: Ligand Dissociation, Basal-Plane Elimination



### Path B: No Ligand Dissociation, Apical-Site Elimination/Direct Transfer



despite the fact that, to date, four-coordinate, Group-10 metal  $\beta$ -chloroalkyl complexes have not been isolated or spectroscopically observed in solution. Indeed, only a few transition metal  $\beta$ -chloroalkyl complexes have been isolated, but none in a system directly relevant to olefin polymerization.<sup>18–20</sup>

Accordingly, herein we present the synthesis and isolation of a  $\beta$ -chloroalkyl complex of square-planar nickel. In addition, we present kinetic decomposition data indicating that an open coordination site within the basal plane of a square-planar complex is not required for  $\beta$ -Cl elimination (Scheme 1, Path B). Our results suggest that significant challenges still remain for the discovery of a viable vinyl chloride coordination–insertion polymerization system with late transition metal catalysts, especially when pathways to the formation of  $\beta$ -chloroalkyls are facile. Importantly, the low-migratory aptitude<sup>21–25</sup> of the perchloroethyl group in our system allows for the study of  $\beta$ -Cl elimination in the absence of competing alkyl-group insertion processes.

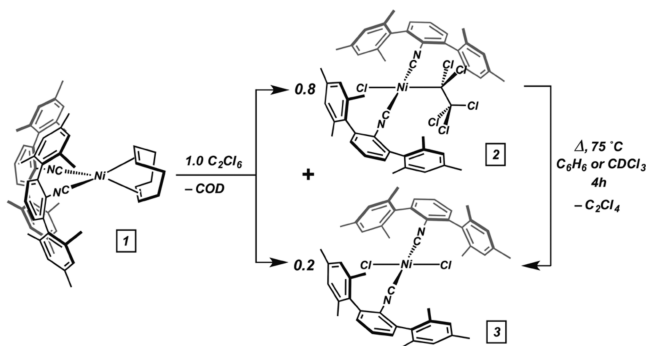
We previously reported the synthesis and characterization of the zero-valent, nickel bis-*m*-terphenyl isocyanide complex

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$\text{Ni}(\text{COD})(\text{CNAr}^{\text{Mes}_2})_2$  (**1**, COD = 1,5-cyclooctadiene;  $\text{Ar}^{\text{Mes}_2}$  = 2,6-(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).<sup>26</sup> Treatment of **1** with 1.0 equiv of hexachloroethane (C<sub>2</sub>Cl<sub>6</sub>) in *n*-pentane solution at room temperature leads to the release of COD and formation of both the pentachloroethyl-chloride complex,  $\text{NiCl}(\text{CCl}_2\text{CCl}_3)(\text{CNAr}^{\text{Mes}_2})_2$  (**2**), and the dichloride complex,  $\text{NiCl}_2(\text{CNAr}^{\text{Mes}_2})_2$  (**3**), in a 4:1 ratio as determined by <sup>1</sup>H NMR spectroscopy (Scheme 2). Dichloride **3** can be completely

Scheme 2. Synthesis and Decomposition of Complex **2**



removed from the mixture by an acetonitrile wash, providing pure, yellow  $\text{NiCl}(\text{CCl}_2\text{CCl}_3)(\text{CNAr}^{\text{Mes}_2})_2$  (**2**) in 79% yield.<sup>27</sup> In  $\text{CDCl}_3$  solution, **2** gives rise to a single set of  $\text{Ar}^{\text{Mes}_2}$  resonances, thereby indicating a trans disposition of isocyanide ligands and rapid rotation about the C–Ni bonds. In addition, the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **2** ( $\text{CDCl}_3$ ) features resonances centered at 66.1 and 88.1 ppm, which are assigned to the  $\alpha$ -CCl<sub>2</sub> and  $\beta$ -CCl<sub>3</sub> carbon atoms, respectively, of the pentachloroethyl ligand. Notably, these resonances are considerably upfield of the <sup>13</sup>C{<sup>1</sup>H} resonance for hexachloroethane ( $\delta$  = 105.4 ppm,  $\text{CDCl}_3$ ), which is consistent with ligation of an ethyl group to a late transition metal center.

Vapor diffusion of *n*-pentane into a saturated fluorobenzene solution of  $\text{NiCl}(\text{CCl}_2\text{CCl}_3)(\text{CNAr}^{\text{Mes}_2})_2$  (**2**) at –35 °C provided single crystals of **2** suitable for analysis by X-ray diffraction. The molecular structure of **2** is shown in Figure 1 and confirms the structural assignment made from solution NMR spectroscopy. In the solid state, the pentachloroethyl unit in **2** adopts a staggered conformation and is located in the cleft formed by the mesityl rings of the two  $\text{CNAr}^{\text{Mes}_2}$  ligands. Most

notably, there are no close contacts between the  $\beta$ -Cl atoms and the Ni center in the solid-state structure of  $\text{NiCl}(\text{CCl}_2\text{CCl}_3)(\text{CNAr}^{\text{Mes}_2})_2$  (**2**). The Ni–Cl4 and Ni–Cl5 distances are 3.3746(16) and 3.4507(14) Å, respectively, which are significantly greater than the most reasonable range for the sum of the covalent radii between Ni and Cl ( $r_{\text{cov}}(\text{Ni}) + r_{\text{cov}}(\text{Cl}) = 2.09$ – $2.26$  Å).<sup>28</sup> In addition, the chlorine atom Cl6 is positioned anti with respect to the Ni1 center along the C3–C4 bond vector and is likewise noninteracting (4.602(2) Å). Interestingly, however, there are close, sub-van der Waals (vdW) contacts between both the  $\alpha$ -Cl and  $\beta$ -Cl atoms of the pentachloroethyl ligand and the  $\pi$ -edge carbons of the proximal mesityl rings of the  $\text{CNAr}^{\text{Mes}_2}$  ligands (Figure 1;  $\Sigma(r_{\text{vdW}}(\text{Cl}) + r_{\text{vdW}}(\text{C}_{\text{aromatic}})) = 3.50$ – $3.64$  Å).<sup>29,30</sup> These contacts, which range from 3.234– $3.515$  Å, are undoubtedly weak if present. However, they may potentially contribute to the stability of  $\text{NiCl}(\text{CCl}_2\text{CCl}_3)(\text{CNAr}^{\text{Mes}_2})_2$  (**2**) in solution and upon crystallization as such, chlorine-to- $\pi$ -edge interactions have been documented to energetically enhance the overall docking of chloro-substituted drug candidates to enzyme active sites.<sup>31–34</sup>

Although a limited number of  $\beta$ -chloroalkyl complexes have been isolated, none have been shown to decompose by a well-defined  $\beta$ -Cl elimination process.<sup>18–20</sup> Furthermore, in systems where facile intramolecular  $\beta$ -Cl elimination is inferred, the corresponding  $\beta$ -Cl alkyl intermediates have not been spectroscopically observed.<sup>4–6,8,13</sup> It is therefore significant that while isolable,  $\text{NiCl}(\text{CCl}_2\text{CCl}_3)(\text{CNAr}^{\text{Mes}_2})_2$  (**2**) can be readily observed to decompose in a manner consistent with intramolecular  $\beta$ -Cl elimination. Heating of either C<sub>6</sub>D<sub>6</sub> or  $\text{CDCl}_3$  solutions of pure  $\text{NiCl}(\text{CCl}_2\text{CCl}_3)(\text{CNAr}^{\text{Mes}_2})_2$  (**2**) at 75 °C results in the formation of the dichloride complex,  $\text{NiCl}_2(\text{CNAr}^{\text{Mes}_2})_2$  (**3**), and small quantities (ca. 10%) of free  $\text{CNAr}^{\text{Mes}_2}$  ligand as determined by <sup>1</sup>H NMR spectroscopy. Analysis of the thermolysis mixture by GCMS and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy indicated the formation of tetrachloroethylene (Cl<sub>2</sub>C=C<sub>2</sub>; TCE) in 91 ± 7% yield (average of 5 runs), thereby suggesting that the formation of dichloride **3** proceeds by a  $\beta$ -Cl elimination mechanism. Importantly, chloroalkane products are not observed after thermolysis (GCMS and <sup>13</sup>C{<sup>1</sup>H} NMR), which indicates that radical-type, homolytic cleavage of the Ni–C<sub>alkyl</sub> linkage is not an operative decomposition pathway for  $\text{NiCl}(\text{CCl}_2\text{CCl}_3)(\text{CNAr}^{\text{Mes}_2})_2$  (**2**). In addition, the free  $\text{CNAr}^{\text{Mes}_2}$  generated during this decomposition process likely arises from thermally induced

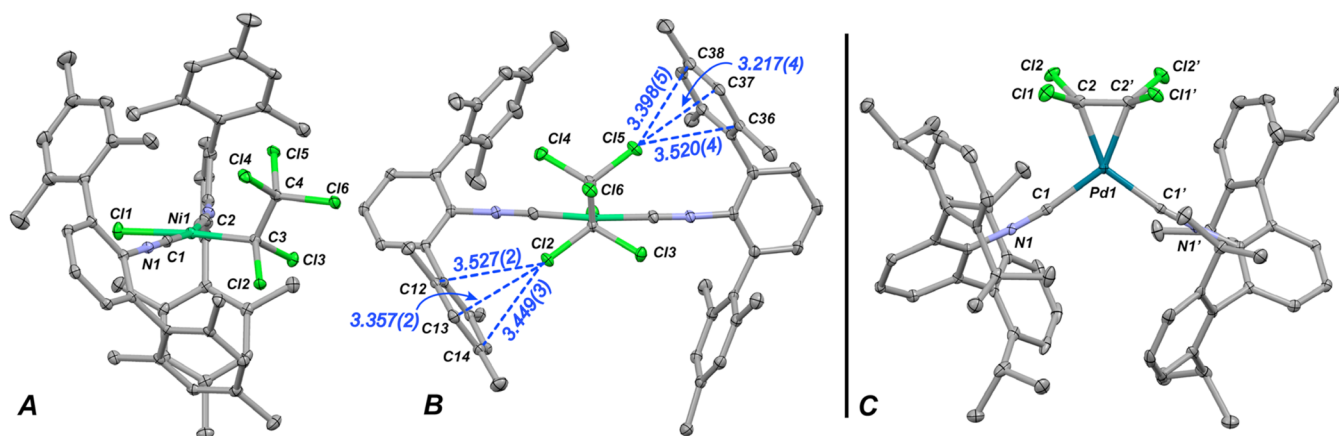


Figure 1. (A) Molecular structure of pentachloroethyl complex **2**. (B) Alternative view of complex **2** highlighting sub-vdW Cl-to- $\pi$ -arene interactions (distances in Å). (C) Molecular structure of the palladium  $\eta^2$ -TCE complex **6**.

isocyanide dissociation from  $\text{NiCl}_2(\text{CNAr}^{\text{Mes}_2})_2$  (**3**) concomitant with the formation of  $[\text{NiCl}_2(\text{CNAr}^{\text{Mes}_2})]_n$  aggregates. As we have previously shown, medium-valent copper-, cobalt- and molybdenum-chloride fragments form particularly labile interactions with *m*-terphenyl isocyanides, which lead to facile isocyanide dissociation processes in solution.<sup>35–37</sup> Thermolysis studies on pure  $\text{NiCl}_2(\text{CNAr}^{\text{Mes}_2})_2$  (**3**) in  $\text{C}_6\text{D}_6$  and  $\text{CDCl}_3$  at 75 °C were consistent with this suggestion and revealed the formation of small quantities of free  $\text{CNAr}^{\text{Mes}_2}$  (ca. 10–15%) over the course of 2–3 h.

The decomposition of  $\text{NiCl}(\text{C}_2\text{Cl}_2\text{CCl}_3)(\text{CNAr}^{\text{Mes}_2})_2$  (**2**) can be readily monitored by  $^1\text{H}$  NMR spectroscopy as a function of time and temperature in  $\text{CDCl}_3$  solution. At 50 °C, 6 and 12 mM solutions of **2** decay reproducibly, within error, with similar observed rate constants (Table S2.3, Supporting Information), thereby indicating an overall first-order process. Eyring analysis of 6 mM solutions of **2** over the temperature range 30–60 °C resulted in activation parameters of  $\Delta H^\ddagger = 19(2)$  kcal/mol and  $\Delta S^\ddagger = -16(6)$  cal/mol·K. The negative  $\Delta S^\ddagger$  of activation for this reaction is particularly noteworthy and indicates an ordered transition state that is inconsistent with a rate-limiting ligand-dissociation event. This suggestion is further corroborated by the fact that the decomposition of **2** is not measurably affected by the addition of up to 8 equiv of free  $\text{CNAr}^{\text{Mes}_2}$  (Table 1).<sup>38</sup>

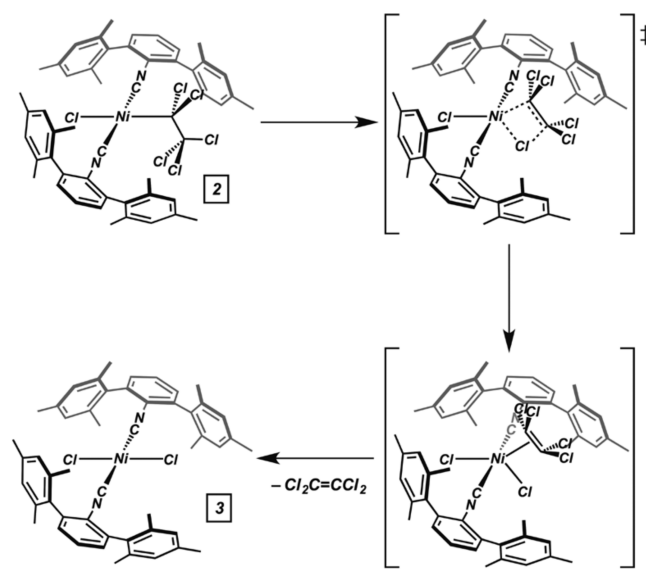
**Table 1. Observed Rate Constants ( $k_{\text{obs}}$ ) for the Decay of Complex **2** (6 mM) in the Presence of Various Additives at 50 °C in  $\text{CDCl}_3$**

additive	equivalents/concentration (mM) additive	$k_{\text{obs}}$ ( $\text{s}^{-1}$ )	error ( $\text{s}^{-1}$ )
none		$1.4 \times 10^{-4}$	$6.8 \times 10^{-6}$
$\text{CNAr}^{\text{Mes}_2}$	0.5/3	$1.1 \times 10^{-4}$	$1.7 \times 10^{-6}$
$\text{CNAr}^{\text{Mes}_2}$	1.0/6	$1.0 \times 10^{-4}$	$5.4 \times 10^{-6}$
$\text{CNAr}^{\text{Mes}_2}$	4.0/24	$2.5 \times 10^{-4}$	$4.9 \times 10^{-6}$
$\text{CNAr}^{\text{Mes}_2}$	8.0/48	$3.0 \times 10^{-4}$	$8.6 \times 10^{-6}$
1-hexene	16.0/96	$8.3 \times 10^{-5}$	$6.2 \times 10^{-6}$
TCE	16.0/96	$2.2 \times 10^{-4}$	$4.8 \times 10^{-6}$

Accordingly, the kinetic data for **2** indicate that  $\beta$ -Cl elimination may not require an in-plane, open coordination site in Group 10 metal polymerization systems. Instead, intramolecular  $\beta$ -Cl elimination may additionally proceed to the apical site of a 16  $e^-$ , square-planar complex. Such a direct transfer mechanism (Scheme 1, Path B), which does not require ligand dissociation, indicates that efforts to increase the rate of olefin binding to a coordinatively unsaturated Group 10  $\beta$ -chloroalkyl complex may not adequately prevent facile  $\beta$ -Cl elimination. Therefore, the only systems appropriate for coordination–insertion polymerization of vinyl chlorides may be those in which the formation of  $\beta$ -chloroalkyl ligands is completely circumvented.<sup>15–17</sup>

With respect to direct transfer of a chloride to the apical site of square-planar Ni, it is important to note that many five-coordinate  $\text{NiX}_2\text{L}_3$  (X = halide) complexes have been reported in the Cambridge Structural Database (CSD; 146 examples; see the Supporting Information). Indeed, when only monodentate L-type ligands are present, structurally characterized  $\text{NiX}_2\text{L}_3$  complexes adopt a trigonal-bipyramidal coordination environment (average  $\tau_5 = 0.75$ ;<sup>39</sup> 10 examples) with equatorial halide ligands. On this basis, we contend that the unobserved dichloride-olefin complex,  $\text{NiCl}_2(\eta^2\text{-C}_2\text{Cl}_4)(\text{CNAr}^{\text{Mes}_2})_2$  (Scheme 3), is a potentially viable intermediate in the decomposition of pentachloroethyl **2** and decays further by

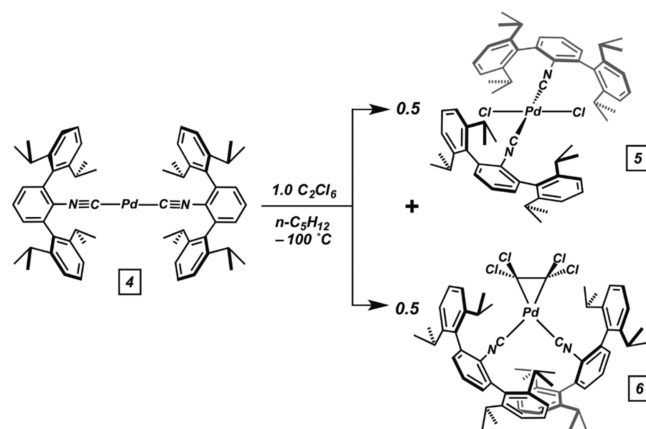
**Scheme 3. Proposed Mechanism of  $\beta$ -Cl Elimination in Complex **2****



dissociation of TCE to dichloride **3**. In addition, the decomposition of **2** at 50 °C is not affected by the presence of excess TCE or 1-hexene (Table 1). These observations provide additional evidence for rate-determining  $\beta$ -Cl elimination from **2** and suggest that the steric properties of the  $\text{CNAr}^{\text{Mes}_2}$  ligands prevent association of olefin substrates such that the rate of  $\beta$ -Cl elimination is not affected.

As a complement to the four-coordinate Ni system represented by **2**, we have also surveyed a related Pd isocyanide system for its ability to provide an isolable  $\beta$ -chloroalkyl complex. Treatment of the Pd(0) bis-isocyanide complex,  $\text{Pd}(\text{CNAr}^{\text{Dipp}_2})_2$  (**4**,  $\text{Ar}^{\text{Dipp}_2} = 2,6\text{-}(2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$ ),<sup>40</sup> with  $\text{C}_2\text{Cl}_6$  (1.0 equiv) at room temperature leads rapidly to the Pd(II) dichloride complex, *trans*- $\text{PdCl}_2(\text{CNAr}^{\text{Dipp}_2})_2$  (**5**). However, when this experiment is repeated at low temperature (ca. –100 °C), an equimolar mixture of dichloride **5** and the  $\eta^2$ -TCE complex,  $\text{Pd}(\eta^2\text{-C}_2\text{Cl}_4)(\text{CNAr}^{\text{Dipp}_2})_2$  (**6**, Scheme 4, Figure 1), is obtained along with 0.5 equiv of unreacted  $\text{C}_2\text{Cl}_6$ . An intermediate pentachloroethyl complex is not spectroscopically observed during this reaction, but the interception of  $\text{Cl}_2\text{C}=\text{CCl}_2$  by the  $\text{Pd}(\text{CNAr}^{\text{Dipp}_2})_2$  fragment suggests that a  $\beta$ -Cl elimination process is likely operative. Furthermore, treatment of Pd-

**Scheme 4. Reaction between Complex **4** and  $\text{C}_2\text{Cl}_6$**



(CNAr<sup>Dipp2</sup>)<sub>2</sub> with 1 equiv of C<sub>2</sub>Cl<sub>6</sub> at low temperature in the presence of 5 equiv of free CNAr<sup>Dipp2</sup> does not alter the product distribution or allow for the observation of an intermediate pentachloroethyl complex. This finding provides circumstantial evidence that isocyanide dissociation is not required prior to  $\beta$ -Cl elimination. Importantly, it has been proposed that five-coordinate, square-pyramidal Pd(II) complexes can serve as fleeting intermediates during methacrylate/ethylene copolymerization catalyzed by Pd(II)  $\alpha$ -diimine complexes.<sup>2,41,42</sup> This suggestion and the results presented here indicate that facile chloride-transfer pathways are accessible to four-coordinate, Group 10 metal  $\beta$ -chloroalkyl complexes without a prior ligand dissociation event.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Synthetic details, kinetic data, and crystallographic results (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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(27) For spectroscopic comparison, the dichloride complex **3** can be prepared independently by treatment of **1** with PCl<sub>5</sub>. See the Supporting Information.

(28) Given the known uncertainty in values for the covalent radii of the transition metals, we present a range for the sum of the covalent radii of Ni and Cl based on several commonly used tabulations (in Å):  $r_{\text{cov}}(\text{Ni}) 1.10 + r_{\text{cov}}(\text{Cl}) 0.99 = 2.09$  (a) Pyykkö, P.; Atsumi, M. *Chem.—Eur. J.* **2009**, *15*, 186. (b)  $r_{\text{cov}}(\text{Ni}) 1.11 + r_{\text{cov}}(\text{Cl}) 0.99 = 2.10$  Batsanov, S. S. *Russ. Chem. Bull.* **1995**, *44*, 2245. (c)  $r_{\text{cov}}(\text{Ni}) 1.24 + r_{\text{cov}}(\text{Cl}) 0.99 = 2.23$ ; *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Cornell, NY, 1960; Chapter 11, p 403. (d)  $r_{\text{cov}}(\text{Ni}) 1.24 + r_{\text{cov}}(\text{Cl}) 1.02 = 2.26$  Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832.

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