

Diaminoarylnickel(II) "Pincer" Complexes: Mechanistic Considerations in the Kharasch Addition Reaction, Controlled Polymerization, and Dendrimeric Transition Metal Catalysts

ROBERT A. GOSSAGE,
LUCIA A. VAN DE KUIL, AND
GERARD VAN KOTEN*

Debye Institute, Department of Metal-Mediated Synthesis,
Utrecht University, Padualaan 8,
3584 CH Utrecht, The Netherlands

Received July 18, 1997

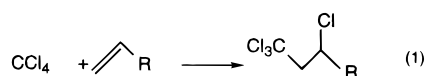
Introduction

It was in 1945 that researchers at the University of Chicago first reported that carbon tetrachloride could be added directly to olefinic double bonds (eq 1). This process was catalyzed by peroxides as radical initiators.¹ This simple reaction is a classic example of anti-Markovnikov addition

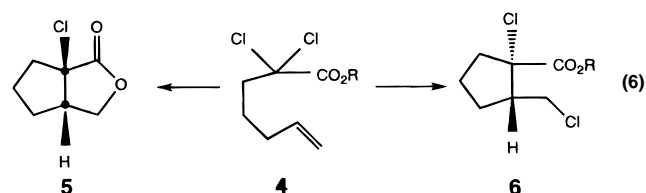
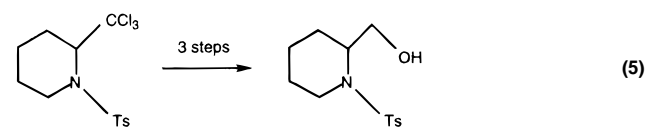
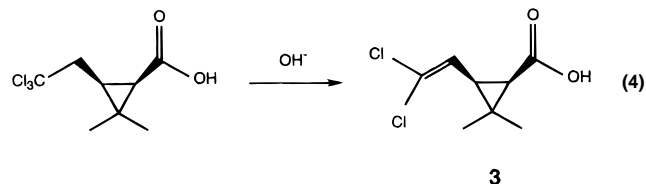
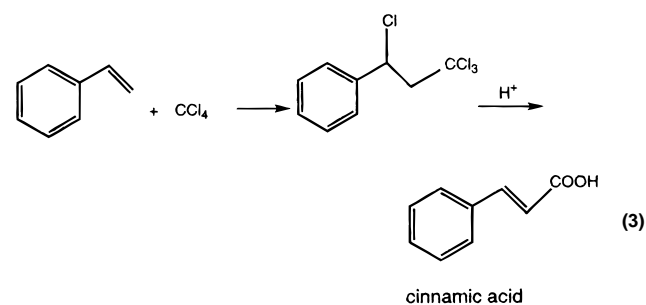
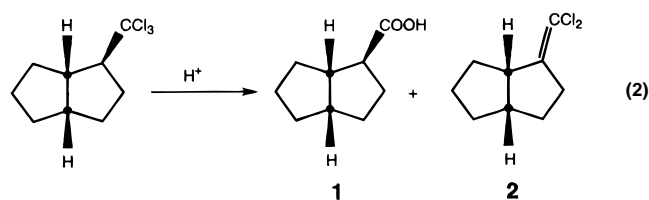
Robert A. Gossage (b. 1965) is a native of Burlington, Ontario, Canada and is a member of the Canadian Institute of Chemistry. He received his B.Sc. degree with a major in chemistry from the University of Guelph, Canada in 1989. After working as a research assistant in the laboratory of Professor E. C. Alyea (Guelph), he joined the group of Professor S. R. Stobart at the University of Victoria, British Columbia, Canada. He completed a Ph.D. degree in 1996 in the areas of ligand design and the stabilization of metal–Si bonds. Since that time he has been a postdoctoral fellow in the group of Professor G. van Koten at the Debye Institute in Utrecht, The Netherlands. His area of interests include multinuclear NMR, organosilicon and organometallic chemistry, and dendrimers.

Lucia A. van de Kuil was born on 25 October 1963 in Utrecht, The Netherlands. She received her diploma Atheneum-B from St. Bonifatius College in Utrecht in 1982. She followed this with an undergraduate study at the Utrecht University and obtained her M.S. C. diploma in 1988. She completed her Ph.D. degree in 1992 also in Utrecht working on mechanistic studies of the Kharasch addition reaction in the groups of Professor Dr. W. Drenth, Professor Dr. L. W. Jenneskens (both of the Department of Physical Organic Chemistry) and Professor Dr. G. van Koten (Department of Metal-Mediated Synthesis). Since 1993 she has been an employee at the Hercules European Research Center B. V. in Barneveld, The Netherlands.

Gerard van Koten obtained his Ph.D. from the Utrecht University (Professor G. J. M. van der Kerk) during his stay in the laboratory for Organic Chemistry (TNO) in Utrecht (1967–1977). After a period in the Inorganic Chemistry Department at the University of Amsterdam, where he was promoted to Professor (1984), he went back to the Utrecht University (Debye Institute) in 1986 to become Professor of Organic Chemistry. He has been Visiting Professor in Strasbourg (France), Heidelberg (Germany), and Sassari (Italy). Research interests comprise the organometallic chemistry of late (Ni, Pd, Pt, Ru) and early transition metals (Ta, La, Lu) as well as of Cu, Li, and Zn, and the development and use of chelating arylamine ("pincer") and aminoarenethiolate bonded organometallic complexes as catalysts for homogeneous catalysis, in particular for fine-chemical synthesis. The preparation and use of the first examples of homogeneous dendrimer catalysts demonstrate his interest for supramolecular systems with (organometallic) catalytically active functionalities.



and has become known as the *Kharasch addition reaction*,² in honor of its discoverer, M. S. Kharasch. In the late 1930s, Kharasch and independently Hey and Waters³ had presented a free-radical mechanism to explain this kind of addition reaction, and it is now generally accepted to occur in this manner.⁴ The use of the Kharasch addition is, however, often overlooked in synthetic organic chemistry although it has been employed in a number of specific syntheses. A few examples of these are shown in eqs 2–6.^{5–7} Both inter- and intramolecular Kharasch addition⁸ is possible.

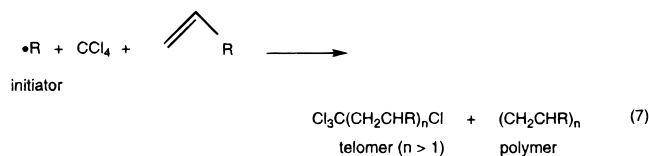


Transition Metal Catalyzed Kharasch Addition

The widespread use of the original free-radical addition is limited because of competing telomerization (i.e.,

* To whom correspondence should be addressed. E-mail: g.vankoten@chem.ruu.nl.

addition of CCl_4 accompanied by alkene coupling to form alkanes) and polymerization reactions (eq 7). By the mid-



1950s, several groups began to investigate the use of transition metal (TM) and other compounds to promote the addition reaction. A number of species were found to *initiate* free-radical addition of polyhalogenated alkanes to alkenes (cf. peroxides); these include $\text{ReCl}_3(\text{PR}_3)_2\text{L}$,⁹ AlMe_3 ,¹⁰ BMe_3 ,¹¹ $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), $\text{Fe}(\text{CO})_5$,¹² and metal dispersions.¹³ Telomerization was still a recurring problem, however. Minisci was among the first to observe that CCl_4 could be added to olefins to yield only the 1:1 adduct.¹⁴ Research has clearly shown that a variety of polyhalogenated compounds (alkyl halides, perfluoroalkyl iodides, and alkylsulfonyl chlorides) can be added across a $\text{C}=\text{C}$ bond.^{5–31} Virtually any olefin can serve as the source of reactive unsaturation. The list of promoters is now quite extensive and includes powdered TM's or inorganic oxides;¹⁵ inorganic halides;^{5d,6,14a,16} mono-,^{12,17} di-,¹⁸ and trinuclear metal carbonyls;¹⁹ cyclopentadienyl and arene complexes;^{18,20,21} metal phosphine compounds;^{8a,9,22–25} Sml_2 ;²⁶ and $\text{RuCl}_2(\text{PPh}_3)_3$ ^{8a,27,28} or its polymer supported analogue.²⁹

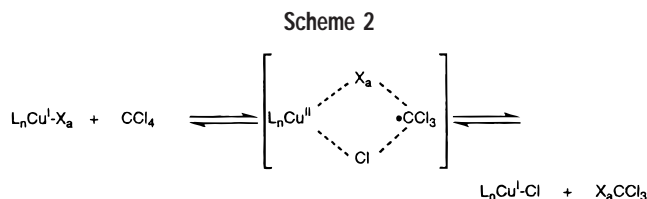
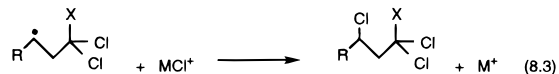
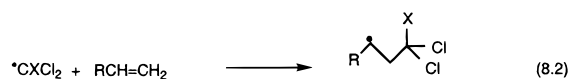
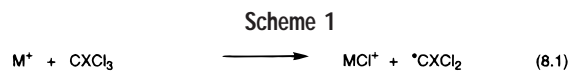
Mechanistic Considerations

The selectivity of the TM catalyzed reactions led Minisci to propose a *redox chain* mechanism for this process.^{14a} A similar idea was presented by Asscher and Vofsi^{30a} to explain the addition of CCl_4 to alkenes promoted by inorganic halides (Scheme 1). This mechanism involves formation of a radical via chloride abstraction by the metal complex (eq 8.1).

Metal chlorides have a much larger chain transfer constant than CCl_4 and thus side reactions are suppressed. The reaction sequence is also encountered in the "atom transfer addition reaction" for C–C bond formation in living radical polymerization reactions.^{31–33}

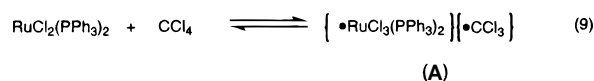
Detailed kinetic studies of this and other systems are sparse. Asscher concluded his work with a kinetic profile of the Cu-catalyzed addition of sulfonyl chlorides to alkenes.^{30c} The redox chain mechanism was found to operate with the olefin having no role in the rate determining step. Nondek and co-workers^{16d} have suggested that free radicals are not released in these systems. They proposed that the CCl_4 unit interacts in a manner depicted in Scheme 2. Support for this type of interaction stems from the observation that when $\text{X}_a = \text{Br}$, bromotrichloromethane is produced when CCl_4 is added in the absence of an olefin.

A later study by Davis on Kharasch catalysis by $[\text{Mo}_2(\text{CO})_6(\eta^5\text{-Cp})_2]$ ($\text{Cp} = \text{cyclopentadienyl}$) and $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_{10}\text{H}_8)]$ revealed that the latter²¹ proceeds via a nonchain sequence whereas the former follows a redox chain



mechanism involving bimetallic radicals. Yields of 1:1 olefin/ CCl_4 adducts are moderate. Later work on related Cp complexes of Fe revealed that a similar mechanism was also operating as the Mo case above.^{18a,20a,b}

One of the most active complexes for the Kharasch addition is the complex $\text{RuCl}_2(\text{PPh}_3)_3$. Both Matsumoto^{27a} and Kamigata^{28a} have described catalysis with this compound as proceeding via "radical reaction in the coordination sphere". This is to signify that the radicals that are generated (e.g., $\bullet\text{CCl}_3$) remain under the influence of the metal center (i.e., "caged" radicals). This concept has been used to rationalize the differences in reactivity between the TM-catalyzed addition and the reaction initiated by peroxides.^{6b,14,27,28} Specifically, this includes product selectivity and the absence of radical coupling products. A detailed mechanistic study of the Ru system was carried out by Davis et al.³⁴ These results suggest that a nonchain pathway takes place with the formation of a coordinated radical pair **A** (eq 9). No evidence for



the coordination of alkene to the metal was found. Thus, it appears that **A** then interacts with the olefin, forming a radical alkyl complex with the halogenated species, chloride being then transferred to the resulting product to regenerate the four coordinate catalytic precursor (see ref 34b). Davis has also presented evidence^{34c} that a common intermediate exists in all Ru phosphine catalyzed Kharasch additions, in contradiction to the beliefs of Matsumoto.^{27a} Several other studies have indicated the formation of coordinated radicals (e.g., **A**) occurs in Cu, Fe, and Mo systems.^{6b,17,20c,30b}

Debate has continued over the mechanism of the Kharasch addition catalyzed by Rh(I) phosphine complexes. White has argued that Rh catalyzed addition is intrinsically different from the other systems based mainly on the fact that the oxidative addition product of the reaction of BrCCl_3 and $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ can be isolated^{25b}

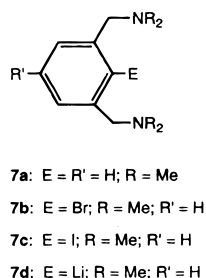


FIGURE 1.

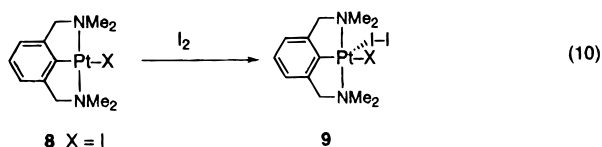
and that chiral Rh systems carry out enantioselective Kharasch addition, as shown by Murai et al.^{25a} Two observations are in conflict with this argument. First, several oxidative addition reactions with complexes of Ir and Pt have been shown to proceed via radical intermediates.³⁵ Thus, oxidative addition products do not rule out a radical mechanism. Second, enantioselectivity has been noted in the Kharasch addition catalyzed by chiral Fe, Ru, and Cu complexes^{16,28b,c} despite mechanistic studies that indicate the presence of caged radicals. The %ee values were moderate in both cases (%ee < 40%). Obviously, the Rh-catalyzed reaction still requires a detailed kinetic analysis to address these contradictions.

Nickel "Pincer" Complexes and the Kharasch Addition Reaction

Over 15 years ago we began a systematic study of multidentate ligands derived from 1,3-[(dimethylamino)methyl]benzene (**7a**) (Figure 1). It was soon realized that complexes could be formed in which the C–R (R = H or halide) fragment on position 2 of the aromatic ring was oxidatively added to a metal center. In addition, transmetalation could also be performed with TM halides if a Li atom was placed in this position (**7d**).

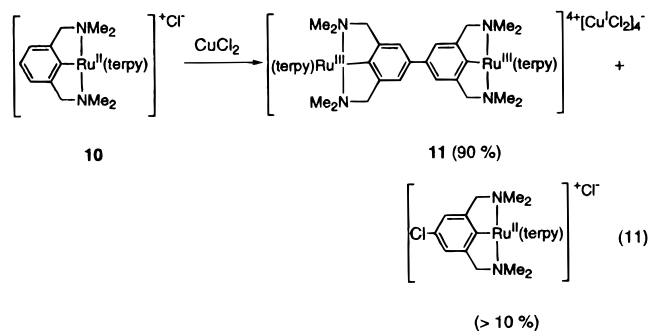
Virtually all TM's will form complexes with **7** and its derivatives, which will hereafter be referred to as (NCN). The chemistry of these ligands has been previously reviewed,³⁶ but a few of the more relevant examples will be presented.

Platinum group metals incorporating (NCN) include the Pt(II) complex [Pt(NCN)X] (**8**; X = Cl, Br, or I).³⁶ These organometallics react with electrophiles such as X₂ or CuX₂ (X = Cl or Br) to form the expected Pt(IV) compounds via an oxidative addition reaction. However, the reaction with I₂ yields the dark purple diamagnetic complex **9**. Spectroscopic data indicate that a Pt(IV) compound is not formed and an X-ray analysis revealed this to be an η¹-I₂ complex. One can assume that this represents the first stage of the reaction of the Pt(II) species with an X₂ unit (eq 10).³⁷



Related compounds (**10**) can be induced to form dimers via Cu-induced coupling of a Ru bound (NCN)

ligand.³⁸ We have used these to study the fundamental properties in molecular "wires" (eq 11).³⁹



The chemistry of nickel (NCN) complexes has also been studied and includes compounds such as [Ni(NCN)X] (**12**) and [Ni(NCN)X₂] (**13**). The (NCN) ligand has been shown to produce stable complexes with the metal in the +II and +III oxidation states. The trivalent compounds were the first stable organometallic Ni(III) complexes to be isolated and fully characterized^{41a} and are air-stable in the solid state. The coordination of the ligand in both cases occurs via two trans chelating Ni–N bonds and a single Ni–C_{aryl} bond. Square planar [diamagnetic; d⁸ Ni(II)]⁴⁰ and square-pyramidal [paramagnetic; d⁷ Ni(III)]⁴¹ geometry is found except in those cases where η⁵-ONCN'O' coordination is found or additional ligands are complexed.^{41b,d} For example, the chiral ligand (NCN)* (Figure 2) contains enantiopure proline groups in the ligand framework. The ester oxygen atom of each proline fragment can coordinate to the metal center in addition to the Ni–C_{aryl} and two Ni–N bonds,^{41d} thus forming an octahedral cationic Ni(III) compound.

An interesting feature of the Ni(II) complexes is their very low oxidation potentials. Typical values for a Ni(II/III) potential is between +0.7 and +1.2 V,⁴² but the Ni-[NCN]X series has much smaller values (+0.14 to +0.57 V).^{41c} Previous work on Cu catalyzed Kharasch addition had demonstrated that a low redox potential was an essential component of the catalyst.^{6b,14a} Until our studies in the late 1980s, we had found no catalytic activity with these Ni complexes. Thus, we examined the reactivity of methyl methacrylate (MMA) with excess CCl₄ in the presence of 5 mol % [Ni(NCN)Cl] in acetonitrile solution. Examination of the products of this combination revealed that after 15 min at room temperature over 90% of the olefin had been converted to the 1:1 CCl₄ adduct.⁴⁴ These are the mildest conditions that have been used in the catalytic Kharasch addition and turnover numbers in excess of 1700 h⁻¹ have been realized. Related complexes require much more forcing conditions. For example, NiCl₂(PR₃)₂ catalyzes the addition of polyhaloalkanes to 1-hexene in low yields and only at temperatures of 140 °C.^{24a,43b} The complex RuCl₂(PPh₃)₃ is one of the most active compounds in promoting the reaction, but is inactive at temperatures below 40 °C.^{23c}

Our early mechanistic studies indicated that the halide ion has little effect in the reaction profile (i.e., selectivity, product yield, turnover number) catalyzed by [Ni(NCN)X]

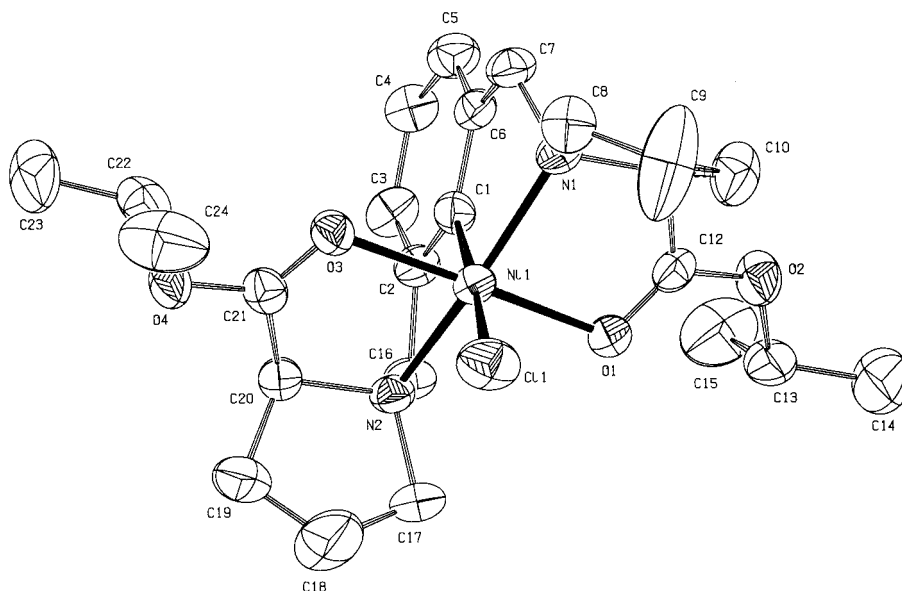


FIGURE 2. ORTEP diagram of the solid-state structure of the octahedral Ni(III) cation $[\text{Ni}(\text{NCN})^*\text{Cl}]^+$. Hydrogen atoms have been omitted for clarity.

($X = \text{halide}$).^{43b} This suggests the presence of a common intermediate. The reaction rate is affected by the nature of the olefin (cf. Cu^{30}) and polyhalogenated alkane.^{43a} We have since performed a detailed kinetic study of this process⁴⁴ and we will thus comment here on our proposed catalytic cycle. Several aspects of the Ni catalysis is similar to that observed in Ni containing *enzyme* systems.

Catalyst "Tuning"

The importance of redox properties on the catalyzed reaction led us to attempt to control this aspect by ligand modification. Our ligand design is quite amenable to adjustment of the electronic and steric components. This was performed in two ways: replacement of two or more of the methyl groups attached to the ligand N atoms by bulkier and more electron-rich fragments and attachment of electron-withdrawing or -releasing groups to the *para* position of the aromatic ring (Figure 1: $R \neq \text{Me}$; $R' \neq \text{H}$).

The effect of bulky groups on the overall molecular geometry of the resulting Ni(II) complexes and their reactivity is severe. Replacement of $R = \text{Me}$ by other groups (e.g., ^iPr) results in significantly longer Ni–N bonds and an overall weaker interaction with the Ni center.⁴⁰ A further result of this substitution is reduced (or no) catalytic activity. This result seems to be steric in nature.^{40c,43b,45}

The influence of *para* positioned groups R' on $[\text{Ni}(\text{C}_6\text{H}_2(\text{CH}_2\text{NMe}_2-2,6)_2-R'-4)\text{X}]$ reveals that electron-donating substituents (e.g., NH_2) cause a reduction in the oxidation potential whereas electron-withdrawing substituents have the opposite effect. This in turn has been shown to affect the reaction rate of the catalytic addition in a linear fashion with respect to the Hammett σ_p constants for the *para*-group.^{40c} The rate increase is proportional to a corresponding lowering of the oxidation potential and indicates that there is an electron demand during the rate-determining step.

Mechanism of the Kharasch Addition Catalyzed by $[\text{Ni}(\text{NCN})\text{X}]$

A systematic variation of a number of components in the reaction was carried out, and the result of each change is listed below.^{43–45}

Product Distribution. The selectivity of this system is very high for alkenes such as MMA with no evidence for any telomeric or polymeric products. This strongly indicates that radicals do not enter the bulk solution. The presence of radicals, i.e., under conditions of a fast back-electron transfer with concomitant atom (halide) transfer, is therefore a strong possibility (reminiscent of **A**, eq 9). A second possibility is that a Ni(IV) oxidative addition product has formed. We favor the former argument since oxidation of Ni(III) to Ni(IV) is very energetically unfavorable.^{40,41a–d,42,43}

Solvent Effects. A variety of solvents were used as the reaction medium and none effectively blocked the catalysis. This indicates that ligating effects are *not* playing any significant role. It should be noted that the corresponding acetonitrile complex $[\text{Ni}(\text{NCN})(\text{CH}_3\text{CN})]^+[\text{BF}_4]^-$ is *inactive* in this reaction despite the presence of a readily available coordination site following dissociation of the bound nitrile. The presence of a halide ligand is thus a necessary component of the catalyst.

Temperature Effects. As expected, the catalytic rate increases with increasing temperature.^{44,45} Unfortunately, a nonlinear effect of the concentration of CCl_4 on the reaction precludes the application of an Arrhenius-type relationship to calculate the exact thermodynamic parameters (below).^{44,45}

Concentration Effects. Variations in concentration of the catalyst and alkene indicated a first-order dependence on these components. However, the effect of variation in concentration of the polyhalogenated alkane CCl_4 closely resembles that observed in Michaelis–Menten kinetics in *enzyme* systems.⁴⁶ The inference here is that

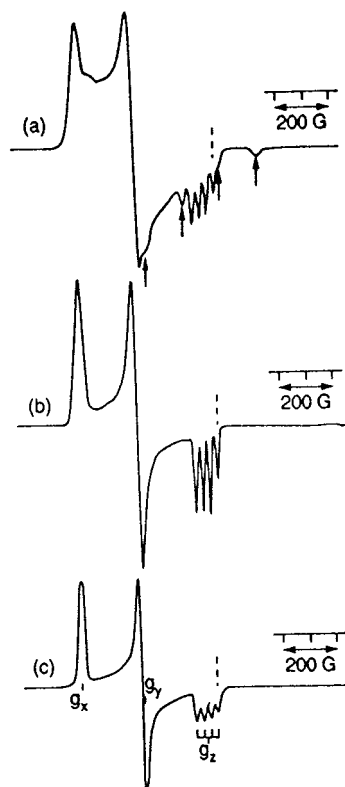
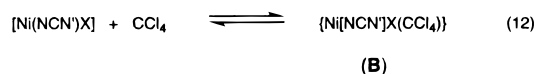


FIGURE 3. X-band ESR spectra of (a) $\text{Ni}^{\text{II}}(\text{NCN})\text{Br}$ mixed with CCl_4 in CH_2Cl_2 . Arrows indicate the g_z tensor with hyperfine coupling due to Br. (b) $\text{Ni}^{\text{II}}(\text{NCN})\text{Br}$ mixed with CCl_4 and MMA in CH_2Cl_2 . Both spectra (a) and (b) were measured at 77 K with $g = 2.0036$ indicated with a dashed line. (c) $\text{Ni}^{\text{III}}(\text{NCN})\text{Cl}_2$ in C_7H_8 glass at 150 K with $g = 2.002$ indicated by the dashed line.

there is a reversible step in the catalytic cycle that involves CCl_4 . A likely situation is that this is a case of saturation kinetics. Thus, the majority of the Ni complexes are probably in the form of a 1:1 adduct (eq 12). Further



evidence for this is provided by the fact that, in the presence of only a slight (e.g., 5-fold) excess of CCl_4 , the Ni complex catalyzes the radical polymerization of alkenes in a highly controlled manner.⁴⁷ Thus, the catalyst serves to activate the polyhalogenated alkane (i.e., by inner-sphere electron transfer), and this alkane will only participate in the reaction profile if it is present in a significant concentration. In our work, the ratio of CCl_4 :Ni is far in excess of 1000:1, and therefore saturation kinetics can be assumed.^{33a}

ESR Evidence. The low-temperature ESR spectra of $[\text{Ni}(\text{NCN})\text{Br}]$ in the presence of CCl_4 , with (during catalysis) and without the presence of MMA, and the corresponding isolated Ni(III) complex $[\text{Ni}(\text{NCN})\text{Cl}_2]$ (**13a**) appear in Figure 3. These spectra provide direct evidence that Ni(III) complexes are formed during catalysis.^{41a-d,44,45} At no time could we observe directly the $\cdot\text{CCl}_3$ radical. Attempts to observe this species in related systems has also proven difficult.^{34a,b,48}

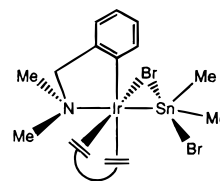


FIGURE 4.

Other Aspects. No adduct could be observed (NMR, IR, ESR) between any alkenyl $\text{C}=\text{C}$ bond and the complex $[\text{Ni}(\text{NCN})\text{Br}]$. We feel that coordination of an alkene is not the first stage of the catalytic cycle. The addition of CCl_4 to a mixture of $[\text{Ni}(\text{NCN})\text{Br}]$ in dichloromethane in the absence of alkene leads to the formation of CBrCl_3 . This confirms that the interaction of the Ni-Br bond with the polyhalogenated alkane is an important fundamental feature (cf., Scheme 2) and that this step is reversible (hence, the saturation kinetic behavior).⁴⁴

The Catalytic Cycle

The proposed catalytic cycle is shown in Scheme 3. The most important aspect of this process is, unlike other systems, that CCl_4 is activated in the absence of a free coordination site and that radicals are bound in the Ni coordination sphere (cf. **A**, eq 9). The word "bound" in this instance refers in kinetic terms to the fact that back-atom electron transfer is much faster than radical combination reactions. These ideas are similar to that proposed by Matsumoto²⁷ and Davis³⁴ but differs in the sequence of events. We feel that the first step involves activation of the polyhalogenated alkane by the Ni(II) complex through an encounter species **B** (eq 12), i.e., an inner-sphere activated complex is formed in which electron transfer occurs, and that this step is reversible.

The formation of **B** is hypothesized to occur when the Ni-X bond serves as an anchor site for a CCl_4 unit forming $\eta^1\text{-Cl}\cdot\text{Ni}$ coordination. This idea has rare but isolated examples in the chemistry of Re,^{49a,b} Ru,^{49c-e} Ir,^{49f,g} and other metals.^{49h,i} This bears obvious relation to the isolation of the $\eta^1\text{-I}_2$ complex **9**. Coordination of the polyhalogenated alkane to the Ni-X fragment may be facilitated by the inherent weakness of the Ni-halide bond. X-ray data of a number of $[\text{Ni}(\text{NCN})\text{Br}]$ complexes⁴⁰ has shown that the Ni-Br bond is longer than in related Ni(II) or Ni(III) complexes.⁵⁰ This is probably a result of the trans-influence of the coordinated aryl unit.⁵¹ The development of a "hypercoordinate" carbon center is perhaps best illustrated in Figure 4 by the five-coordinate Sn(IV) center of $[\{2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\}(\text{COD})\text{Ir}(\text{Br})\text{SnMe}_2\text{-Br}]$.^{52,53}

The forward association with intermediate **B** containing the radical is assumed to be rate-determining and explains the first-order dependence of alkene. We have no evidence for the final stage of the catalytic cycle, but it is assumed that halide transfer to the organic radical occurs with concomitant reduction of the Ni(III) complex back to the Ni(II) "resting" state, followed by elimination of the 1:1 adduct from the metal coordination sphere.

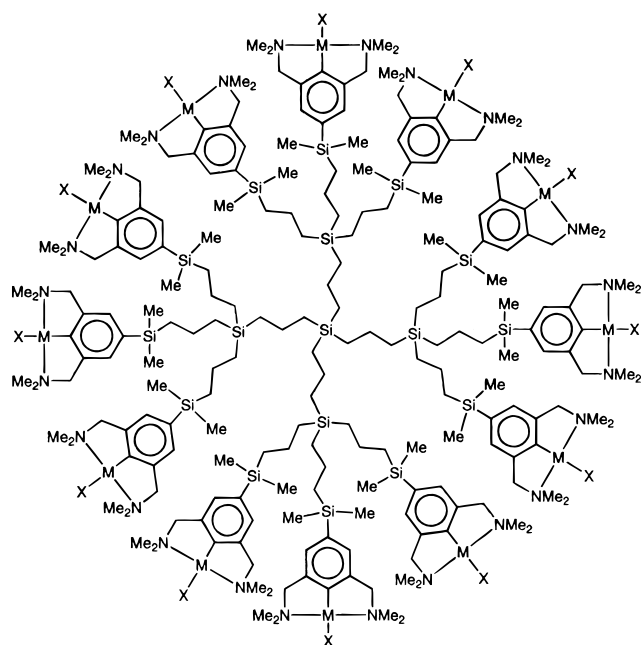
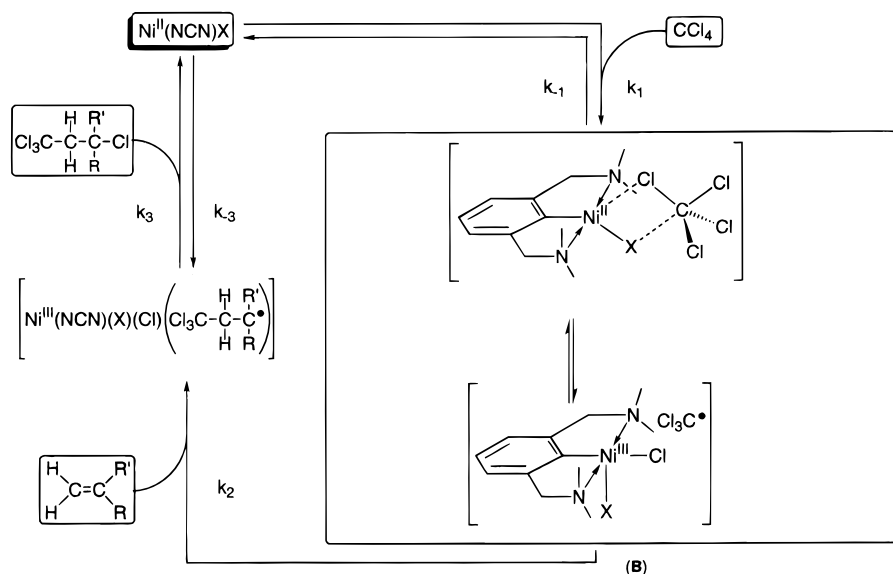
Scheme 3. The Proposed Catalytic Cycle for the 1:1 Kharasch Addition of CCl_4 to MMA Catalyzed by $\text{Ni}(\text{NCN})\text{X}$ 

FIGURE 5. An example of a carbosilane (**G1**) dendrimer appended by $[\text{M}(\text{NCN})\text{X}]$ transition metal catalysts ($\text{M} = \text{Ni}, \text{Pt}; \text{X} = \text{Cl}, \text{Br}, \text{I}$).

This catalytic system presents a rare example where substrate concentrations can be used to alter the reaction profile and hence the products.^{43,47} In the presence of a large excess of polyhalogenated alkane, 1:1 Kharasch addition is the only reaction that occurs.^{43–45} If a stoichiometric amount of this halocarbon is used, then it serves to initiate the catalyst for controlled radical olefin polymerization.⁴⁷ Thus, changes in $[\text{CCl}_4]$ could be used to arrest alkene polymerization and induce the addition of CCl_3 fragments (via Kharasch addition) to the terminus of the polymer in situ (this assumes kinetic control of the reaction where $k_{\text{Kharasch}} \gg k_{\text{polymerization}}$ if $[\text{CCl}_4] \gg [\text{catalyst}]$).⁵⁴ This procedure should facilitate recovery of the catalyst since it is released from the polymer end-groups.

$\text{Ni}[\text{NCN}]\text{X}$: an "Artificial Enzyme"?

Proteins containing Ni were isolated in the early 1980s.⁵⁵ Although enzyme systems contain complex structures, there are some similarities between these compounds and $[\text{Ni}(\text{NCN})\text{X}]$. The observation of saturation kinetics (cf. Michaelis–Menten) in the reversible coordination of CCl_4 to $[\text{Ni}(\text{NCN})\text{X}]$ is obviously reminiscent of enzyme–substrate complexes.^{31,46} A unique property of Ni-containing proteins and enzymes is the observation of a low oxidation potential of the Ni(II/III) redox couple.⁵⁵ This was first reported by Lancaster in membrane-bound Ni from the Archaeobacterium *Methanobacterium bryantii*.^{56a} Later, Ni(III) complexes were discovered in Ni hydrogenase enzymes obtained from the related species *Methanobacterium thermoautotrophicum*^{56b} and *Desulfovibrio gigas*.^{56c} The presence of a Ni(III) metal center was confirmed by labeling experiments.⁵⁶ Of further relevance is that Ni enzymes such as urease *also carry out Kharasch addition* in aqueous media.⁵⁷ It is tempting to say that we are mimicking a biological catalyst, but it is of interest to see a purely synthetic system that can perform the same chemical reactions as isolated enzymes.

Design of "Dendrimer Catalysts"

We have also studied our catalysts when they are bound to well-defined organic supports. These materials can be used as heterogeneous catalysts or as soluble species which can be removed from the reaction stream by filtration or other techniques. This work includes the incorporation of $[\text{Ni}(\text{NCN})\text{X}]$ catalysts onto polysiloxane polymers.^{58a} These macromolecules can be easily recovered but in no way sacrifice their catalytic activity in the Kharasch addition. Similarly, the $[\text{Ni}(\text{NCN})\text{X}_2]$ compounds can be grafted onto silica particles for use as models of colloids with a covalently bound paramagnetic surface layer.^{58b} Perhaps our most interesting result is the first "dendrimer catalyst" to be designed and tested. Den-

drimers are monodispersed macromolecules that are generally synthesized by a repetitive reaction series.⁵⁹ We have attached the [Ni(NCN)X] unit onto the exterior of a carbosilane dendrimer⁶⁰ (Figure 5) and have tested these materials in the Kharasch addition reaction.^{58c} Catalytic activity is maintained and the loss of the active nickel complex by catalyst "leaching" is almost impossible as this would require Ni–C bond cleavage. In addition, the dendrimer retains its high solubility in organic solvents. We are currently expanding this chemistry and will report the details of this shortly.⁶¹

Thanks to all of our co-workers who worked with so much energy and dedication on this subject: Dr. D. M. Grove who, with Drs. R. Zoet and W. P. Mul, first discovered the *d*⁷ Ni(III) organometallics and all those whose names are found in refs 36b and 37–41. The authors are indebted to Drs. M. Albrecht and A. L. Spek for providing the ORTEP diagram for Figure 2. We would thank the following organizations for their continued support of this research: European Union, Utrecht University, SON/NWO, and Ciba-Geigy.

References

- (1) (a) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *Science* **1945**, *102*, 128. (b) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *J. Am. Chem. Soc.* **1945**, *67*, 1626. (c) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *J. Am. Chem. Soc.* **1946**, *68*, 154–155. (d) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *J. Am. Chem. Soc.* **1947**, *69*, 1100–1105. (e) Kharasch, M. S.; Reinmuth, O.; Urry, W. H. *J. Am. Chem. Soc.* **1947**, *69*, 1105–1110.
- (2) In some circles this process is called the *Prins Reaction*, but this term often causes confusion with respect to the addition of formaldehyde to olefins, which is also referred to as the Prins reaction. See: March, J. *Advanced Organic Chemistry*, 4th ed.; John-Wiley & Sons: London, 1992; Section 5–33. Kharasch addition is an example of what is currently being referred to as "Atom Transfer Radical Addition" (ATRA).
- (3) Hey, D. H.; Waters, W. A. *Chem. Rev.* **1937**, *21*, 169–208.
- (4) Kharasch, M. S.; Engelmann, H.; Mayo, F. R. *J. Org. Chem.* **1938**, *2*, 288–302.
- (5) Dowbenko, P. *J. Am. Chem. Soc.* **1964**, *86*, 946–947.
- (6) (a) Rijnenbrij, P. P. M.; Loven, R.; Wijnberg, J. B. P. A.; Speckamp, W. N.; Huisman, H. O. *Tetrahedron Lett.* **1972**, 1425–1428. (b) Bellus, D. *Pure Appl. Chem.* **1985**, *57*, 1827–1838. (c) Martin, P.; Steiner, J.; Winkler, T.; Bellus, D. *Tetrahedron* **1985**, *41*, 4057–4078. (d) Martin, P.; Streith, J.; Rihs, G.; Winkler, T.; Bellus, D. *Tetrahedron Lett.* **1985**, *26*, 3947–3950.
- (7) Klemmensen, P. D.; Kolind-Andersen, H.; Madsen, H. B.; Svendsen, A. *J. Org. Chem.* **1979**, *44*, 416–420.
- (8) (a) Hayes, T. M.; Villani, R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 5533–5543 and references therein. (b) Nagashima, H.; Ara, K.; Wakamatsu, H.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1985**, 518–519. (c) Nagashima, H.; Wakamatsu, H. *J. Chem. Soc., Chem. Commun.* **1984**, 652–653. (d) Matsumoto, H.; Ohkawa, K.; Ikemori, S.; Nakamo, T.; Nagai, Y. *Chem. Lett.* **1979**, 1011–1014. (e) Takano, S.; Nishizawa, S.; Akiyama, M.; Ogasawara, K. *Heterocycles* **1984**, *22*, 1179–1188. (f) Nagashima, H.; Wakamatsu, H.; Itoh, K.; Tomo, Y.; Tsuji, J. *Tetrahedron Lett.* **1983**, *24*, 2395–2398.
- (9) Grigg, R.; Devlin, J.; Ramasubbu, A.; Scott, R. M.; Stevenson, P. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1515–1520.
- (10) Maruoka, K.; Sano, H.; Fukutani, Y.; Yamamoto, H. *Chem. Lett.* **1985**, 1689–1691.
- (11) Takeyama, Y.; Ichinose, Y.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1989**, *30*, 3159–3162.
- (12) Freidlina, R. Kh.; Velichko, F. K. *Synthesis* **1977**, 145–154.
- (13) See, for example: Kondakov, S. E.; Smirnov, V. V. *Kinet. Catal.* **1995**, *36*, 315–319.
- (14) (a) Minisci, F. *Acc. Chem. Res.* **1975**, *8*, 165–171. (b) Also see: Fouassier, J. P.; Rabek, J. F., Eds. *Radiation Curing in Polymer Science and Technology*. Vol. II: *Photoinitiating Systems*; Elsevier: London, 1993; Chapter 6.
- (15) (a) Steiner, E.; Martin, P.; Bellus, D. *Helv. Chim. Acta* **1982**, *65*, 983–985. (b) Badanyan, Sh. O.; Voskanyan, M. G.; Chobanyan, Zh. O. *Russ. Chem. Rev.* **1981**, *50*, 1074–1086 and references therein. (c) Vit, Z.; Hájek, M. *Collect. Czech. Chem. Commun.* **1987**, *52*, 1280–1292 and references therein. (d) Laurent, P.; Blancou, H.; Commeyres, A. *J. Fluorine Chem.* **1993**, *64*, 125–127 and references therein.
- (16) (a) Murai, S.; Tsutsumi, S. *J. Org. Chem.* **1966**, *31*, 3000–3003. (b) Burton, D. J.; Kehoe, L. J. *J. Org. Chem.* **1971**, *36*, 2596–2599 and references therein. (c) Mitani, M.; Nakayama, M.; Koyoma, K. *Tetrahedron Lett.* **1980**, *21*, 4457–4460. (d) Nondek, L.; Hun, L. G.; Wicherlová, B.; Krupicka, S. *J. Mol. Catal.* **1987**, *42*, 51–55. (e) Afanas'ev, I. B.; Samokhvalov, A. *Russ. Chem. Rev.* **1969**, *38*, 318–329 and references therein. (f) Kitora, M.; Adámek, F.; Hájek, M. *Catal. Lett.* **1993**, *18*, 345–348 and references therein. (g) Hirao, T.; Ohshiro, O. *Synlett* **1990**, 217–218. (h) Boutevin, B.; Dongala, E. B. *Tetrahedron Lett.* **1977**, 4315–4316.
- (17) Hogeveen, H.; Elzinga, J. *J. Org. Chem.* **1980**, *45*, 3957–3969.
- (18) (a) Davis, R.; Groves, I. F. *J. Chem. Soc., Dalton Trans.* **1982**, 2281–2287. (b) Davis, R.; Durrant, J. L. A.; Khazaal, N. M. S.; Bitterwolf, T. E. *J. Organomet. Chem.* **1990**, *386*, 229–239.
- (19) Fuchikami, T.; Ojima, I. *Tetrahedron Lett.* **1984**, *25*, 307–308.
- (20) (a) Davis, R.; Khazaal, N. M. S.; Maistry, V. *J. Chem. Soc., Chem. Commun.* **1986**, 1387–1389. (b) Kerber, R. C.; Waldbaum, B. R. *J. Organomet. Chem.* **1996**, *513*, 277–280.
- (21) Davis, R.; Khazal, N. M. S.; Bitterwolf, T. E. *J. Organomet. Chem.* **1990**, *397*, 51–58.
- (22) Ishihava, T.; Kuroboshi, M.; Okada, Y. *Chem. Lett.* **1986**, 1895–1896.
- (23) Nagashima, H.; Tsuji, J.; Sato, K. *Tetrahedron* **1985**, *41*, 393–397 and references therein.
- (24) (a) Inoue, Y.; Ohno, S.; Hashimoto, H. *Chem. Lett.* **1978**, 367–368. (b) Saushkina, T. P.; Zubritskii, L. M.; Petrova, A. A. *Zh. Org. Khim.* **1990**, *26*, 722–725.
- (25) (a) Murai, S.; Sugise, R.; Sonada, N. *Angew. Chem.* **1981**, *93*, 481–482. (b) Cable, C. J.; Adams, H.; Bailey, N. A.; Crosby, J.; White, C. *J. Chem. Soc., Chem. Commun.* **1991**, 165–166. (c) Pereira, S.; Srebnik, M. *J. Am. Chem. Soc.* **1996**, *118*, 909–910.
- (26) Ma, S.; Lu, X. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2031–2033 and references therein.
- (27) (a) Matsumoto, H.; Motegi, T.; Nakano, T.; Nagai, Y. *J. Organomet. Chem.* **1979**, *174*, 157–161 and references therein. (b) Sasson, Y.; Rempel, G. L. *Synthesis* **1975**, 448–450. (c) Derouet, D.; Brosse, J. C. *Eur. Polym. J.* **1991**, *27*, 537–547.

- (28) (a) Kameyama, M.; Kamigata, N.; Kobayashi, M. *J. Org. Chem.* **1987**, *52*, 3312–3316 and references therein. (b) Kameyama, M.; Kamigata, N. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 648–650. (c) Kamigata, N.; Fukushima, T.; Terakawa, Y.; Yoshida, M.; Sawada, H. *J. Chem. Soc., Perkin Trans. 1* **1991**, 627–633 and references therein.
- (29) Phelps, J. C.; Bergbreiter, D. E.; Lee, G. M.; Villani, R.; Weinreb, S. M. *Tetrahedron Lett.* **1989**, *30*, 3915–3918.
- (30) (a) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1961**, 2261–2264, **1963**, 1887–1896, 3291–3297. (b) Asscher, M.; Vofsi, D. *J. Chem. Soc. B* **1968**, 947–952. (c) Asscher, M.; Vofsi, D. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1000–1002.
- (31) Minisci, F., Ed. *Free Radicals in Organic Synthesis and Biology*; Kluwer: Dordrecht, The Netherlands, 1989.
- (32) (a) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674–680. (b) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866–868. (c) Webster, O. W. *Science* **1991**, *251*, 887–893. (d) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* **1997**, *30*, 2190–2193. (e) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970–7972.
- (33) (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: London, 1978; pp 197–203. (b) Tsuji, J. *Organic Synthesis by Means of Transition Metal Complexes*; Springer-Verlag: Heidelberg, 1975; pp 61–64.
- (34) (a) Bland, W. J.; Davis, R.; Durrant, J. L. A. *J. Organomet. Chem.* **1984**, *267*, C45–C48. (b) Bland, W. J.; Davis, R.; Durrant, J. L. A. *J. Organomet. Chem.* **1985**, *280*, 397–406. (c) Davis, R.; Furze, J. D.; Cole-Hamilton, D. J.; Pogorzelec, P. *J. Organomet. Chem.* **1992**, *440*, 191–196.
- (35) (a) Bradley, J. S.; Connor, D. E.; Dolphin, D.; Labinger, J. A.; Osborn, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 4043–4044. (b) Labinger, J. A.; Kramer, A. V.; Osborn, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 7903–7904. (c) Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Chem. Commun.* **1973**, 948–949. (d) Hargreaves, N. G.; Puddephatt, R. J.; Sutcliffe, L. H.; Thompson, P. J. *J. Chem. Soc., Chem. Commun.* **1973**, 861–862. (e) Also see: Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527–2532.
- (36) (a) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681–1694. (b) Rietveld, M. H. P.; Grove, D. M.; van Koten, G. *New J. Chem.* **1997**, *21*, 751–771.
- (37) (a) van Beek, J. A. M.; van Koten, G.; Stufkens, D. J.; van der Linden, J. G. M. *J. Am. Chem. Soc.* **1986**, *108*, 5010–5011. (b) van Koten, G. *Pure Appl. Chem.* **1990**, *62*, 1155–1159.
- (38) Sutter, J. P.; Grove, D. M.; Beley, M.; Collin, J.-P.; Veldman, N.; Spek, A. L.; Sauvage, J.-P.; van Koten, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1282–1284.
- (39) (a) James, S. L.; Veldman, N.; Spek, A. L.; van Koten, G. *Chem. Commun.* **1996**, 1309–1310. (b) Davis, P. J.; Veldman, N.; Grove, D. M.; Spek, A. L.; Lutz, B. T. G.; van Koten, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1959–1961. (c) Steenwinkel, P.; James, S. L.; Grove, D. M.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 513–515. (d) Davis, P. J.; Grove, D. M.; van Koten, G. *Organometallics* **1997**, *16*, 800–802. (e) Lagunas, M.-C.; Gossage, R. A.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 731–741.
- (40) (a) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Zoet, R.; Spek, A. L. *Organometallics* **1984**, *3*, 1003–1009. (b) van Beek, J. A. M.; van Koten, G.; Ramp, M. J.; Coenjaarts, N. C.; Grove, D. M.; Goubitz, K.; Zoutberg, M. C.; Stam, C. H.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1991**, *30*, 3059–3068. (c) van de Kuil, L. A.; Luitjes, H.; Grove, D. M.; Zwikker, J. W.; van der Linden, J. G. M.; Roelofsen, A. M.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1994**, *13*, 468–477. (d) van de Kuil, L. A.; Veldhuizen, Y. S. J.; Grove, D. M.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 267–277. (e) Schimmelpfennig, U.; Zimmering, R.; Scheinitz, K. D.; Stösser, R.; Wenschuh, E.; Baumeister, U.; Hartung, H. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1931–1938.
- (41) (a) Grove, D. M.; van Koten, G.; Zoet, R.; Murrall, N. W.; Welch, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 1379–1380. (b) Grove, D. M.; van Koten, G.; Mul, W. P.; van der Zeijden, A. A. H.; Terheijden, J.; Zoutberg, M. C.; Stam, C. H. *Organometallics* **1986**, *5*, 322–326. (c) Grove, D. M.; van Koten, G.; Mul, P.; Zoet, R.; van der Linden, J. G. M.; Legters, J.; Schmitz, J. E. J.; Murrall, N. W.; Welch, A. J. *Inorg. Chem.* **1988**, *27*, 2466–2473. (d) van de Kuil, L. A.; Veldhuizen, Y. S. J.; Grove, D. M.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1995**, *488*, 191–197. (e) For related Ni(III) compounds containing only Ni–C bonds, see: Alonso, P. J.; Falvello, L. R.; Forníes, J.; Martín, A.; Menjón, B.; Rodríguez, G. *Chem. Commun.* **1997**, 503–504.
- (42) Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77–119.
- (43) (a) Grove, D. M.; van Koten, G.; Verschuuren, A. H. M. *J. Mol. Catal.* **1988**, *45*, 169–174. (b) Grove, D. M.; Verschuuren, A. H. M.; van Koten, G.; van Beek, J. A. M. *J. Organomet. Chem.* **1989**, *372*, C1–C6.
- (44) van de Kuil, L. A.; Grove, D. M.; Gossage, R. A.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1997**, *16*, 4985–4994.
- (45) van de Kuil, L. A. Ph.D. Thesis (Proefschrift), Universiteit Utrecht, 1993.
- (46) Stryker, L. *Biochemistry*; Freeman Publishing Co.: San Francisco, 1981; pp 103–184.
- (47) Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1996**, *29*, 8576–8582.
- (48) Connor, J. A.; Riley, P. I. *J. Chem. Soc., Dalton Trans.* **1979**, 1318–1323.
- (49) (a) Winter, C. M.; Veal, W. R.; Garner, C. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 4766–4776. (b) Peng, T.-S.; Winter, C. H.; Gladysz, J. A. *Inorg. Chem.* **1994**, *33*, 2534–2542. (c) Pathak, D. D.; Adams, H.; White, C. J. *J. Chem. Soc., Chem. Commun.* **1994**, 733–734. (d) Conroy-Lewis, F. M.; Redhouse, A. D.; Simpson, S. J. *J. Organomet. Chem.* **1989**, *366*, 357–367. (e) Kulawiec, R. J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **1990**, *9*, 745–755. (f) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970–1973. (g) Burk, M. J.; Segmüller, B.; Crabtree, R. H. *Organometallics* **1987**, *6*, 2241–2246. (h) Van Seggan, D. M.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1992**, *31*, 2987–2990. (i) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89–115 and references therein.
- (50) (a) Lehmkuhl, H.; Näser, J.; Mehler, G.; Keil, T.; Danoski, F.; Benn, R.; Mynott, R.; Schroth, G.; Gabor, B.; Krüger, C.; Betz, P. *Chem. Ber.* **1991**, *124*, 414–425. (b) Schmitt, H.-J.; Weidenhammer, K.; Ziegler, M. L. *Chem. Ber.* **1976**, *109*, 2558–2564. (c) Krüger, C. *Chem. Ber.* **1976**, *109*, 3574–3580. (d) Cámpora, J.; Gutiérrez, E.; Poveda, M. L.; Ruiz, C.;

- Carmona, E. *J. Chem. Soc., Dalton Trans.* **1992**, 1769–1774. (e) Scatturin, V.; Tureo, A. *J. Inorg. Nucl. Chem.* **1958**, 447–451. (f) Stalick, J. K.; Ibers, J. A. *Inorg. Chem.* **1970**, 9, 453–458.
- (51) (a) Jackson, S. A.; Eisenstein, O.; Martin, J. D.; Albeniz, A. C.; Crabtree, R. H. *Organometallics* **1991**, 10, 3062–3069. (b) McWeeny, R.; Mason, R.; Towl, A. D. C. *Faraday Discuss. Chem. Soc.* **1969**, 47, 20–25. (c) Basolo, F.; Pearson, R. G. *Prog. Inorg. Chem.* **1962**, 4, 381–453. (d) Grünberg, A. A. *Acta Physicochim. URSS* **1935**, 3, 573–576; *Bull. Acad. Sci. URSS, Cl. Sci. Chem.* **1943**, 350–356.
- (52) van der Zeijden, A. A. H.; van Koten, G.; Wouters, J. M. A.; Wijsmuller, W. F. A.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1988**, 110, 5354–5361.
- (53) Preliminary molecular modelling studies (MM2 and ZINDO) have shown that such a hypercoordinate carbon species is a viable intermediate: Grove, D. M. Unpublished results.
- (54) For an example of block copolymer synthesis via "living" carbocationic followed by "living" radical polymerization, see: Coca, S.; Matyjaszewski, K. *Macromolecules* **1997**, 30, 2808–2810. This form of polymerization is also called "Atom Transfer Radical Polymerization" (ATRAP); see ref 2.
- (55) Thomson, A. J. *Nature* **1982**, 298, 602–603.
- (56) (a) Lancaster, J. R., Jr. *FEBS Lett.* **1980**, 115, 285–288. (b) Albracht, S. P. J.; Graf, E.-G.; Thauer, R. K. *FEBS Lett.* **1982**, 140, 311–313. (c) Cammack, R.; Patil, D.; Aguirre, R.; Hatchikian, E. C. *FEBS Lett.* **1982**, 142, 289–292.
- (57) Kitazume, T.; Ikeya, T. *J. Org. Chem.* **1988**, 53, 2350–2352. The authors of this article incorrectly refer to urease as a "porphyrin" enzyme. The Ni centers in this enzyme are thought to be in a pseudo-octahedral geometry and ligated by five N and/or O donor atoms and a single S atom. Although urease carries out Kharasch-type addition, there is no evidence that this enzyme contains a Ni center in the +3 oxidation state or that urease is involved in any form of redox cycle during catalysis (unlike the hydrogenases and membrane-bound Ni compounds discussed above). Therefore, the mechanism of action of this enzyme must be distinctly different from that of the [Ni(NCN)X] complexes described in this Account (see: (i) Cammack, R. *Catalysis by Nickel in Biological Systems*. In *Bioinorganic Catalysis*; Reedijk, J. Ed., Marcel Dekker: New York, 1993; Chapter 7. (ii) Finnegan, M. G.; Kowal, A. T.; Werth, M. T.; Clark, P. A.; Wilcox, D. E.; Johnson, M. K. *J. Am. Chem. Soc.* **1991**, 113, 4030–4032. (iii) Clark, P. A.; Wilcox, D. E.; Scott, R. A. *Inorg. Chem.* **1990**, 29, 579–581). We thank the comments of the reviewers in this area.
- (58) (a) van de Kuil, L. A.; Grove, D. M.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Chem. Mater.* **1994**, 6, 1675–1683. (b) Pathmamanoharan, C.; Wijkens, P.; Grove, D. M.; Philipse, A. P. *Langmuir* **1996**, 12, 4372–4377. (c) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, 372, 659–663.
- (59) (a) Fréchet, J. M. J. *Science* **1994**, 263, 1710–1715. (b) Tomalia, D. M. *Sci. Am.* **1995**, 272, 62–68.
- (60) (a) Roovers, J.; Zhou, L. L.; Toporowski, P. M.; van der Zwan, M.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, 26, 963–968 and references therein. (b) van der Made, A. W.; van Leeuwen, P. W. N. M.; de Wilde, J. C.; Brandes, R. A. C. *Adv. Mater.* **1993**, 5, 466–468 and references therein.
- (61) (a) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G.; Gossage, R. A.; Kleij, A. W.; Kragl, U.; Brinkmann, N. Manuscript in preparation. (b) Kleij, A. W.; Gossage, R. A.; Kleijn, H.; van Koten, G.; Kragl, U.; Brinkmann, N. KNCV Katalyse Symposium, May 12–13, 1997, Kerkrade, The Netherlands, poster 37. (c) Kragl, U.; Dreisbach, C.; Wandrey, C. In *Applied Homogeneous Catalysis with Organometallic Compounds*, Cornils, B., Herrmann, W. A., Eds. Vol. 2; VCH: Weinheim, 1996; Chapter 3.2.3.

AR970221I