Mechanistic Aspects of the Kharasch Addition Reaction Catalyzed by Organonickel(II) Complexes Containing the Monoanionic Terdentate Aryldiamine Ligand System [C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-R-4]$^{-}$[†]

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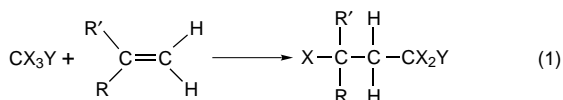Leonardus W. Jenneskens,[§] Wiendelt Drenth,[§] and Gerard van Koten[*,‡]

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The addition reaction of polyhalogenated alkanes to alkenes (Kharasch addition reaction) is homogeneously catalyzed in the absence of O$_2$ under mild reaction conditions (25 °C) by the arylnickel complexes [Ni^{II}\{C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-R-4\}Br] (R = H, MeC(O), Cl, MeO, NH$_2$) and shows a high selectivity for the 1:1 adduct. Kinetic data on the catalytic system with [Ni\{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6\}Br] (R = H; abbreviated as [Ni(NCN)Br]), methyl methacrylate, and CCl$_4$ reveal a rate of reaction that is first order in nickel complex and in alkene. In our series of *para*-substituted arylnickel catalysts, the rate of catalysis increases with the electron donating character of the *para* substituents on the aryl ligand and this rate correlates directly with the Ni^{II}/Ni^{III} redox potential. These data, together with separate spectroscopic studies and results from individual experiments employing other solvents, other polyhalogenated alkanes such as CBr$_4$ and CF$_3$CCl$_3$ and other alkene substrates such as styrene, 1-octene, and cyclohexene, lead to the proposal of a catalytic cycle based on a nonchain mechanism with a mononuclear nickel species. Before or in the rate-determining step oxidation of the Ni(II) center to a d^7 arylnickel(III) species occurs by a single electron transfer and halide transfer from the polyhalogenated alkane in an inner-sphere activated complex [Ni(NCN)-(μ-Cl)CCl$_4$]. This step generates an organic radical intermediate which is proposed to stay in the coordination sphere of the metal where it reacts with the alkene. The reaction rate decreases with an increase in the steric congestion at the N-donor centers in derivatives of the [Ni(NCN)Br] catalyst (*i.e.*, NMe$_2$ > NEt$_2$ > NMe(*i*-Pr) > NMe(*t*-Bu)). This behavior is consistent with the characteristics for an inner-sphere electron-transfer process. Selective 1:1 Kharasch product formation then results from a chain transfer in the Ni(III) coordination sphere by the reverse process, *i.e.*, single electron transfer with concomitant halide transfer. Important conclusions of this study are that the initially active site of the catalyst is the Ni−X unit (X = halide) and that activation of CCl$_4$ occurs in the absence of a free coordination site.

Introduction

The generation of carbon−carbon bonds is an important reaction step in organic synthesis. One way to form such a bond and, thus, extend a carbon chain is by the addition of a polyhalogenated alkane to an alkene substrate to form a 1:1 adduct, as shown in eq 1. This

$$CX_3Y + \ \underset{R}{\overset{R'}{C}}=\underset{H}{\overset{H}{C}}H \longrightarrow X-\underset{R}{\overset{R'}{\underset{|}{C}}}-\underset{H}{\overset{H}{\underset{|}{C}}}-CX_2Y \qquad (1)$$

X = halogen; Y = H, halogen, CF$_3$, or other electronegative group

type of reaction is generally known as the Kharasch addition reaction,[1] and in addition to the formation of a new carbon−carbon σ-bond, synthetically useful halide

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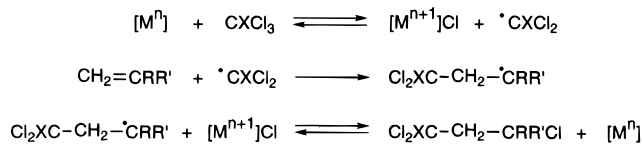[§] Department of Physical Organic Chemistry.

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substituents are introduced at the same time. The application of such 1:1 adducts as synthetic intermediates has been reviewed.[2] The Kharasch addition reaction requires either a free radical precursor as the promotor or a metal complex as the catalyst. The reaction has been extensively investigated both for synthetic purposes and for mechanistic information. The classical free radical chain mechanism is operative not only with initiators such as light, heat, and peroxides,[1] but also with a variety of metal complexes.[3] With certain substrates, it can be difficult to select for the

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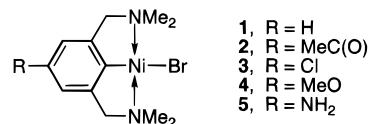
Scheme 1

$$[M^n] + CXCl_3 \rightleftharpoons [M^{n+1}]Cl + {}^{\bullet}CXCl_2$$

$$CH_2=CRR' + {}^{\bullet}CXCl_2 \longrightarrow Cl_2XC-CH_2-{}^{\bullet}CRR'$$

$$Cl_2XC-CH_2-{}^{\bullet}CRR' + [M^{n+1}]Cl \rightleftharpoons Cl_2XC-CH_2-CRR'Cl + [M^n]$$

Kharasch addition because of radical stability or activity which leads to chain propagation and, thus, the formation of 1:2 adducts, telomers and/or polymers. The prerequisite for selective 1:1 addition is, thus, controlled chain termination. For metal-complex-catalyzed reactions, the two principal types of mechanisms are primarily discriminated by the role of the metal species.

The first type of mechanism (Scheme 1) involves the inclusion of a redox system into the propagation steps of the conventional free radical chain addition. The metal complex then participates both in the initiation and in the chain propagation as a halogen transfer agent, in its oxidized form being a much more reactive halogen donor than the polyhalogenated alkane.[4] This reaction sequence is commonly encountered in the so-called atom transfer radical addition (ATRA) reactions for C–C bond formation in organic synthesis,[5,6] as well as in controlled living radical polymerization by atom transfer polymerization (ATRAP).[7] This redox chain mechanism has been postulated for copper and iron halides as catalysts.[4a-i]
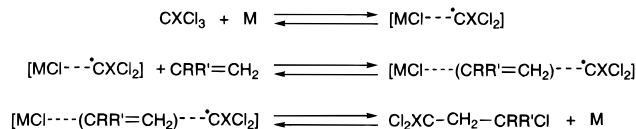
In the second type of Kharasch addition, the mechanism proceeds *via* a non-chain pathway as depicted in Scheme 2.[8] The organic radicals that result from a single electron transfer (SET) between the metal complex and a polyhalogenated alkane are more-or-less 'caged' in the coordination sphere of the metal species. Matsumoto *et al.*[8a-e] and Davis *et al.*[8g] have proposed

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Figure 1. Square-planar arylnickel complexes [Ni^{II}{C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-R-4}Br], **1**–**5**. Complex **1** is abbreviated as [Ni(NCN)Br].

Scheme 2

$$CXCl_3 + M \rightleftharpoons [MCl\text{-}\text{-}{}^{\bullet}CXCl_2]$$

$$[MCl\text{-}\text{-}{}^{\bullet}CXCl_2] + CRR'=CH_2 \rightleftharpoons [MCl\text{-}\text{-}\text{-}\text{-}(CRR'=CH_2)\text{-}\text{-}\text{-}{}^{\bullet}CXCl_2]$$

$$[MCl\text{-}\text{-}\text{-}\text{-}(CRR'=CH_2)\text{-}\text{-}{}^{\bullet}CXCl_2] \rightleftharpoons Cl_2XC-CH_2-CRR'Cl + M$$

such a mechanism for Kharasch catalysis with complexes of the general formula [MCl$_2$(PPh$_3$)$_x$] (M = Ru, x = 3; M = Ni, x = 2). Recent studies into applications and mechanisms of the complex-catalyzed Kharasch addition reaction with a variety of metal species[9] have included a suggestion of another type of mechanism involving oxidative addition of a polyhalogenated alkane to a rhodium(I) complex.[9g]

Earlier studies in this laboratory[10] have shown that the arylnickel(II) complex [Ni{C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-R-4}Br] (R = H; **1**), depicted in Figure 1, is an active homogeneous catalyst for the Kharasch addition reaction with a range of polyhalogenated alkanes (*e.g.,* CCl$_4$, CBr$_4$, and CF$_3$CCl$_3$) and a variety of terminal alkenes (*e.g.,* methyl methacrylate, styrene, and 1-octene) under mild reaction conditions.[10,11] Furthermore, we have used the substituent R to graft the arylnickel moiety not only to polysiloxane polymers[12a] and silica[12b] but also on to carbosilane dendrimers[13] and have shown that some of these new (water and organic solvent) soluble materials possess good catalytic activity.[12a,13]

Recently, as an extension of the metal-catalyzed Kharasch addition reaction, Sawamoto *et al* reported that certain metal complexes can homogeneously polymerize methyl methacrylate (MMA) in the presence of low concentrations of XCCl$_3$ (X = Cl, Br) in aromatic media. This process is catalyzed by either [RuCl$_2$-(PPh$_3$)$_3$][7b,c] or [NiX$_2$(PR$_3$)$_2$][7j] in the presence of a Lewis

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acid activator, and the experimental data and product composition point to a controlled radical polymerization in both of these systems. An essential difference between this polymerization reaction and the 1:1 Kharasch addition reaction is that polymerization is performed using almost equimolar concentrations of the polyhalogenated alkane and the metal catalyst, whereas a Kharasch addition is typically performed under conditions where the metal is used in a 0.01−10 mol % quantity relative to the polyhalogenated alkane (and alkene substrate). The controlled radical polymerization concept has been extended by Matyjaszewski and co-workers[7d,e] for the bulk polymerization of styrene and MMA. This process uses a CuX/2,2′-bipyridine catalyst which is similar to many of the Cu halide/amine systems that are used in Kharasch addition reactions.[2−4] A recent report by Teyssié and collaborators details the similar use of the arylnickel(II) complex (**1**), first synthesized in this laboratory,[14,15a] in a similar manner for a well-controlled radical polymerization of MMA at rather moderate temperatures.[7h] This report is highly relevant to the interpretation of the new results reported herein.

The present study of the Kharasch addition reaction is primarily aimed at acquiring information about the fundamental steps and mechanism of the catalytic cycle that is operative when [Ni^{II}{C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-R-4}X] complexes are used as catalysts. These compounds have a number of features that distinguish them from the other metal catalysts previously used to probe the mechanism of this reaction. In particular, monoanionic ligands of the type [C$_6$H$_2$(CH$_2$NR′R″)$_2$-2,6-R-4]$^-$ usually enforce a terdentate *N,C,N*-coordination geometry at a metal center.[14] Their Ni(II) complexes generally have a square-planar metal geometry with the direct M−C$_{aryl}$ σ-bond flanked by two, mutually trans-positioned, ortho-chelating, tertiary amino substituents. The group X is trans to the aryl unit.[15] We have already reported that the *para*-substituent (R) influences the Ni(II)/Ni(III) redox potential in such aryldiaminenickel(II) complexes[16] and we have shown that other modifications of the ligand system can influence (through both steric and electronic factors) both catalysis[11,15c] and ligand coordination modes.[15b]

In this investigation of the Kharasch addition reaction, kinetic experiments have been undertaken using the *para*-substituted aryldiaminenickel(II) complexes [Ni{C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-R-4}Br] (R = H, MeC(O), Cl, MeO, NH$_2$; **1−5**),[16] depicted in Figure 1, with MMA as the alkene substrate and CCl$_4$ as the polyhalogenated alkane. An important aspect of this catalytic system is that under the ATRA conditions employed (*i.e.,* a high polyhalogenated alkane/Ni catalyst ratio), there is *exclusive formation of the 1:1 Kharasch addition prod-*

ucts, *i.e.* telomerization or polymeric products are not formed.[7h] Supplementary spectroscopic and mechanistic experiments with other polyhalogenated alkanes (*e.g.,* CBr$_4$ and CF$_3$CCl$_3$) and other alkene substrates (*e.g.,* cyclohexene and 1-octene) have been used to provide further information regarding the elementary steps of the catalytic process and the nature of possible intermediates. The results show that catalysis is based on a mononuclear nickel species and that the oxidation potential of Ni(II)/Ni(III) plays an important role. The catalytic cycle we propose involves as a characteristic feature the activation of the polyhalogenated alkane directly at a Ni−X bond rather than in a vacant coordination site.

Results

The Catalytic System 1/MMA/CCl$_4$ and Its Products. The combination of [Ni^{II}{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}-Br], **1**, abbreviated as [Ni(NCN)Br], as the catalyst with MMA as the alkene substrate, CCl$_4$ as the polyhalogenated alkane, and CH$_2$Cl$_2$ as the inert solvent at 25 °C is a highly reactive catalytic system for the Kharasch addition reaction. Total turnover numbers of 1700 are possible with this combination of reagents, and initial turnover frequencies of around 400 h^{-1} are observed.[10,11] All the materials of this catalytic system are easily handled, and the 1:1 addition product, 2,4,4,4-tetrachloro-2-methylbutanoic acid methyl ester, can be readily analyzed by GLC. It should be stressed, however, that this catalytic system is O$_2$ sensitive, and thus, all kinetic and mechanistic studies have been carried out under an inert (N$_2$) atmosphere.

The ^{1}H NMR spectra and GC analysis of the volatiles from the reaction of MMA with CCl$_4$ using [Ni(NCN)-Br] as the catalyst under various conditions show the predominant product to invariably be the 1:1 adduct with a reaction selectivity of more than 99%. In none of the experiments was there any evidence found for the formation of telomeric or polymeric materials (*cf.,* ref 7h). Since free radical polymerization of MMA, which is easily initialized by transition metal complexes[17] and light,[18] is known to be fast,[17−20] the absence of such products already directly points to catalysis occurring by a non-free-radical type of mechanism in which the metal complex plays a central role.[7h] In this system, a small amount of 2-*bromo*-4,4,4-trichloro-2-methylbutanoic acid methyl ester (less than 0.3%) is formed as a byproduct in the first 5−10 min. Since the bromine atom can only originate from the [Ni(NCN)Br] catalyst, this means that the halide atom of the catalyst is intimately involved in the catalytic process.

Kinetics and Thermodynamic Parameters of the Catalytic System 1/MMA/CCl$_4$. In the kinetic studies, three series of experiments were carried out in which the reaction rate was measured with varying concentrations of the reactants, namely: (i) the arylnickel(II) complex **1**, (ii) the alkene MMA, and (iii) the polyhalogenated alkane CCl$_4$ (see Supporting Information).

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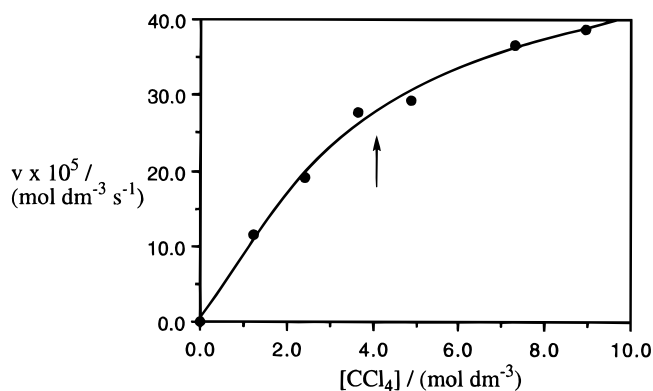
Figure 2. Variation of the initial reaction rate with CCl_4 concentration; MMA (3 mL), [Ni(NCN)Br] (30 mg, 9.1×10^{-5} mol) in CH_2Cl_2 (total volume of 25.5 mL). The arrow indicates the $[CCl_4]$ under the standard catalytic conditions (see Experimental Section).

Table 1. Temperature and Solvent Effects on the Rate Constants for Reaction of MMA with CCl_4 Catalyzed by 1[a]

solvent	T (K)	$E_T{}^b$	$k \times 10^5$ (s^{-1})[c]
dichloromethane	283.3	41.1	7.3
	293.4	41.1	17.4
	298.5	41.1	30.7
	303.7	41.1	42.4
	313.2	41.1	86.0
diethyl ether	298.2	34.6	15.9
tetrahydrofuran	298.2	37.4	25.0
pyridine	298.2	40.2	55.1
acetonitrile	298.2	46.0	136.1
methanol	298.2	55.5	42.6

[a] Reaction conditions: MMA (3 mL), CCl_4 (10 mL), [Ni(NCN)Br], **1**, (30 mg, 9.1×10^{-5} mol), and solvent (12.5 mL). [b] E_T values as a measure for solvent polarity taken from ref 18. [c] $k = k_T \times [CCl_4] \times$ [Ni(NCN)Br]; Eyring equation: $\ln(k_T/T) = \ln(k_B/h) + \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT$ with k_B = Boltzmann's constant and h = Planck's constant.

In the first series of experiments, the concentration of nickel complex **1** was varied. A linear plot of the rate constants determined vs the concentration of **1** indicates a first-order dependence in the arylnickel(II) complex catalyst. Secondly, the rate of conversion of MMA as a function of time was determined under conditions where an excess of CCl_4 was present. The plot of the natural logarithm of the concentration of MMA vs time showed distinctly linear behavior indicating a first-order dependence in MMA. Finally, in the third series of experiments, the concentration of CCl_4 was varied and the initial rate of reaction determined. When these rates are plotted against CCl_4 concentration (Figure 2), one obtains a nonlinear relationship. This behavior resembles that encountered with Michaelis-Menten kinetics for enzymes.[21] However, this type of rate dependence can also be explained by *saturation kinetics* involving prior formation of an adduct radical of the type $\{[Ni^{III}(NCN)X_2](Cl_3C^{\bullet})\}$ (X = Cl, Br). In this scheme, there is increased competition between the termination (chain-transfer) reaction of the $Cl_3C^{\bullet}$ radical (by concomitant electron and halide transfer) and the 1:1 adduct radical with MMA, the latter being the overall forward reaction (product forming step). *The inference here is that there is a reversible step in the catalytic cycle that involves the [Ni(NCN)X] catalyst and CCl_4.* Recall that under conditions of low CCl_4 concentration, living radical polymerization of MMA is the dominant reaction.[7h] For both polymerization and 1:1 Kharasch addition, the polyhalogenated alkane is activated by the catalyst and will, therefore, only appear in the reaction (product) profile if it is present in sufficient quantity. We believe that this activation phenomenon is due to reversible coordination of the CCl_4 unit to the Ni catalyst (above), a concept which will be discussed in more detail below.

Preliminary results[11] indicated that the polarity of the reaction medium exerts a pronounced effect on the reaction rate of the [Ni(NCN)Br]-catalyzed Kharasch addition reaction. In the present study, the effects of several solvents, varying from diethyl ether to methanol, on the reaction rate were investigated more quantitatively, and these results are listed in Table 1. These results clearly show that none of these very different solvents block the catalytic cycle, and in general, increasing the polarity of the reaction medium has a positive effect on the reaction rate. The correlation found by plotting the polarity of the solvent (E_T values from Reichardt[22]) vs the reaction rate is, however, only moderate. When the polarity of the medium is changed in a controlled way by adding various amounts of CH_3-CN to the standard catalytic system, where CH_2Cl_2 is the solvent, then a plot of the rate constant against the reaction medium composition shows a linear dependence, *i.e., ligating effects of CH_3CN (and by inference other solvents) are not playing any significant role in the catalytic cycle.*

Spectroscopic Studies of 1 with Alkenes and Polyhalogenated Alkanes. To understand the catalytic cycle of the Kharasch addition reaction, it is necessary to have information on the separate interactions of the catalyst **1** with the alkene substrate and the polyhalogenated alkane.

A likely interaction of the metal complex with an olefin is η^2-alkene coordination. To investigate this possibility, solutions of **1** with added terminal alkenes (*e.g.,* MMA, styrene, and 1-octene) were studied under various conditions using IR and NMR spectroscopies. The data showed no evidence for η^2-coordination of the alkene functionality to the metal complex in solution. However, with MMA, the IR data do point to η^1-*O*-coordination between the alkene's carbonyl function and the metal complex. When an excess of **1** is added to an MMA solution, the C=O stretch absorption band of MMA at 1720 cm^{-1} shifts to 1580 cm^{-1}. This lowering of the C=O band frequency arising from coordination of a carbonyl functionality to a metal center is well recognized.[23a] We have also recently found when using other arylnickel(II) complexes as catalysts in the Kharasch addition reaction that the presence of ester functionalities on the nitrogen donor substituents can block catalysis and lead to the formation of stable ionic arylnickel(III) complexes having intramolecular η^1-*O*-coordination.[24]

(21) (a) For a general discussion, see: Stryer, L. *Biochemistry*; Freeman: San Francisco, 1981; pp 103−184. (b) Isaacs, N. S. *Physical Organic Chemistry*; Longman: 1987; pp 624−641.

(22) (a) Reichardt, C.; Harbusch-Görnert, E. *Liebigs Ann. Chem.* **1980**, 721. (b) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH Verlagsgesellschaft GmbH: Weinheim, 1988; pp 285−338. (c) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.
(23) (a) Hesse, M. *Spectroscopic Methods in Organic Chemistry*; George Thieme Verlag: Stuttgart, 1987. (b) Connor, J.; Riley, P. I. *J. Chem. Soc., Dalton Trans.* **1979**, 1318.

The possibility of a particular interaction of the metal complex catalyst with the polyhalogenated alkane can be inferred from the fact that the bromine atom of [Ni-(NCN)Br], **1**, does become incorporated into the 1:1 Kharasch addition product. An earlier observation that the ionic species [Ni{$C_6H_3(CH_2NMe_2)_2$-2,6}(CH_3CN)]BF_4 does not catalyze the Kharasch addition reaction had already emphasized the importance of a metal−halide functionality in the catalyst (*vide infra*).[7h,10,11] Significantly, analysis by GLC and GC-MS of a mixture of **1** alone with CCl_4 (1:1) in CH_2Cl_2 revealed that $CBrCl_3$ had been formed, and this confirms that interaction of the Ni−Br bond of **1** and CCl_4 is an important fundamental feature. This conclusion is in line with the kinetic results obtained on the catalytic system where saturation of the catalytically active site by excess CCl_4 occurs. These GLC and GC-MS analyses also showed the absence of hexachloroethane (that can arise from the combination of two $Cl_3C^\bullet$ radicals), and this is extra evidence that the interaction and further reaction between the nickel complex and carbon tetrachloride does not follow a free radical pathway. This implies that efficient reversible transfer of the $Cl_3C^\bullet$ radical occurs by single electron/halide transfer at a [$Ni^{III}(NCN)X_2$] site to regenerate the [$Ni^{II}(NCN)X$] catalyst and Cl_3CX.

Since Ni(II) complexes [Ni(NCN)X] are readily oxidized by X_2 or CuX_2 to the corresponding stable Ni(III) complexes [Ni(NCN)X_2] (X = Cl, Br or I),[25] there was a distinct possibility that the interaction of **1** with CCl_4 might afford paramagnetic Ni(III) complexes that could be detected by ESR spectroscopy. First, the ESR spectrum of a mixture of **1** and CCl_4 in CH_2Cl_2 was measured at low temperature (see Figure 3a). Second, an active catalytic reaction mixture consisting of MMA, CCl_4, and **1** in CH_2Cl_2 was investigated. After catalysis had been running for a few minutes, a sample of the solution was taken and transferred to an ESR tube (under N_2 atmosphere), which was immediately cooled with liquid nitrogen. This mixture gave, at 77 K, the spectrum depicted in Figure 3b. For comparative purposes, the ESR spectrum of an authentic sample of [$Ni^{III}(NCN)Cl_2$] is shown in Figure 3c. The ESR spectra of square-pyramidal complexes [$Ni^{III}(NCN)X_2$] can be interpreted in terms of a low-spin d^7 Ni(III) system with the unpaired electron in a d_{z^2} orbital which is involved in bonding with an apical halide atom.[25] The remarkable similarity between the spectra of Figures 3a,b and that of 3c proves that Ni(III) species are present in the mixtures containing **1** and CCl_4. In the spectrum of Figure 3a, the g_z tensor pattern can be seen to arise from two overlapping signals with different hyperfine couplings, *viz.* 27 and 141 G. These values for the hyperfine coupling are in agreement with those found for [Ni^{III}-$(NCN)Cl_2$] (28 G) and [$Ni^{III}(NCN)Br_2$] (140 G).[25b] We conclude, therefore, that a mixture of **1** and CCl_4 alone is able to produce Ni(III) species containing chloro and bromo ligands. Note that the ESR hyperfine coupling only reflects the nature of the apical halide and that ESR tensor values are not sufficiently sensitive to the basal halide to allow discrimination of the dihalo species
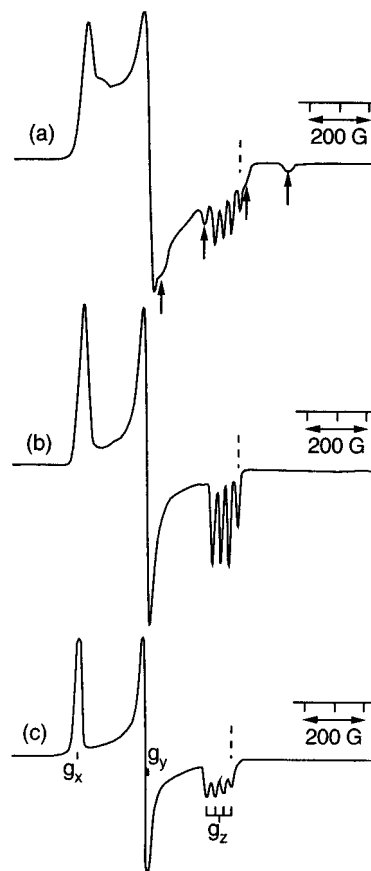

Figure 3. X-band ESR spectra of (a) [Ni^{II}{$C_6H_3(CH_2$-$NMe_2)_2$-2,6}Br] mixed with CCl_4 in CH_2Cl_2. Arrows indicate the g_z tensor with hyperfine coupling due to bromide. (b) [Ni^{II}{$C_6H_3(CH_2NMe_2)_2$-2,6}Br] mixed with CCl_4 and MMA in CH_2Cl_2. The spectra a and b were measured at 77 K with $g = 2.0036$ indicated with a dashed line. (c) [Ni^{III}{$C_6H_3(CH_2NMe_2)_2$-2,6}Cl_2] in toluene glass at 150 K with $g = 2.002$ indicated by the dashed line.

[Ni(NCN)$X_{apical}X_{basal}$] from mixed species [Ni(NCN)-$X_{apical}Y_{basal}$] (X and Y can be Cl or Br) which may also be present. Furthermore, when a Ni(III) complex [Ni-(NCN)X_2] is formed, one would also expect the concomitant formation of a $Cl_3C^\bullet$ radical, but we have been unable to find any evidence for the latter.[23b] As a final point, it must be stressed that the intensities of the Ni-(III) ESR signals obtained from the catalytic mixture have not been quantified, and at this stage we cannot definitively say whether these signals are directly associated with intermediates in the predominating catalytic cycle.

Catalysis Using 1 with Other Alkenes and Polyhalogenated Alkanes. The comparative reactivity of several alkene substrates determined using CCl_4 as the polyhalogenated alkane and **1** as the catalyst are listed in Table 2. The catalyzed addition reactions of these alkenes, like that of MMA, are regiospecific and anti-Markovnikov with, in general, high selectivity for formation of the 1:1 adduct.

The reactivity can be interpreted in terms of steric hindrance and resonance stability of the radical intermediates. For example, 1,2-disubstituted alkenes have a low reactivity that is probably determined by steric hindrance. Resonance stability seems to play a role in affording a higher reactivity for MMA than for methyl

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Table 2. Comparison of the Reactivity of Several Alkenes[a]

substrate	[Cat]/[Alkene] (%)	conversion[b] (%)	$k \times 10^5$ (s^{-1})	selectivity for 1:1 adduct[b]
methyl methacrylate	0.32	65[c]	29.8	100
styrene	0.35	56[c]	22.2	100
methyl acrylate	0.33	23[c]	6.6	100
1-octene	0.32	13[c]	3.9	100
cyclohexene	0.31	12[d]	0.04	86[e]
methyl crotonate	0.32	2[d]	f	100
dimethyl maleate	0.33	0[d]		
dimethyl fumarate	0.33	0[d]		

[a] Reaction conditions: CCl$_4$ (10 mL), [Ni(NCN)Br] (30 mg, 9.1 × 10^{-5} mol), and CH$_2$Cl$_2$ (12.5 mL) at 25 °C. [b] Conversion determined by GLC and selectivity by GLC and GC-MS. [c] Conversion determined after 1 h. [d] Conversion determined after 24 h. [e] The 1:1 adduct is formed in a *cis*/trans ratio of 1:2; side products formed: 12% 3-chlorocyclohexene and 12% CHCl$_3$. [f] Value not determined.

Table 3. Competition Experiments: Methyl Methacrylate (MMA) *versus* 1-Octene[a]

exp no.	substrate ratio MMA:1-octene[b]	$k \times 10^5$ (s^{-1}) MMA	$k \times 10^5$ (s^{-1}) 1-octene
1	1:0	33.5 ± 1.2	
2	0:1		3.9 ± 0.5
3	9:1	33.9 ± 2.8	2.8 ± 0.2
4	1:9	41.3 ± 2.4	4.1 ± 0.2
5	1:1	38.4 ± 0.7	3.2 ± 0.2

[a] Reaction conditions: CCl$_4$ (10 mL), [Ni(NCN)Br] (30 mg, 9.1 × 10^{-5} mol), and CH$_2$Cl$_2$ (12.5 mL) at 25 °C. [b] Total alkene concentration is constant (1.1 mol / L).
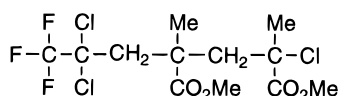
Figure 4. The 1:2 adduct obtained from the reaction of CCl$_3$CF$_3$ with MMA.

acrylate. Only with the internal alkene cyclohexene (that affords primarily the *cis* and *trans* 1:1 adducts in a 1:2 ratio) is there a significant formation of byproducts, namely 3-chlorocyclohexene and chloroform (in an approximate 1:1 ratio). Chloroform could arise from allylic hydrogen abstraction by a Cl$_3$C$^\bullet$ radical, and a subsequent reaction between the resulting cyclohexenyl radical and CCl$_4$ could generate 3-chlorocyclohexene (and a Cl$_3$C$^\bullet$ radical).[1h] The significance of this result is discussed later.

To gain further insight into the role of the alkene in this catalytic system, competition experiments were performed using a 1:1 mixture of a more reactive alkene, MMA, and a less reactive alkene, 1-octene. No products other than the expected 1:1 adducts of these two alkenes were observed with GLC. The observed rate constants of this mixed system are given in Table 3; compared to the pure alkenes, one sees that there is a slight increase of the rate constant for MMA and a corresponding slight decrease of that for 1-octene.

Several polyhalogenated compounds have also been tested in the Kharasch addition reaction with **1** as the catalyst and MMA as the alkene substrate. The following order of decreasing reactivity was found: CBrCl$_3$ > CBr$_4$ > CCl$_4$ > CCl$_3$CF$_3$, and all of these compounds except CCl$_3$CF$_3$ show an excellent selectivity for formation of a 1:1 adduct; with CBrCl$_3$, the product is 2-bromo-4,4,4-trichloro-2-methylbutanoic acid methyl ester. In the case of CCl$_3$CF$_3$, the slowest reacting polyhalogenated compound, one obtains together with the major 1:1 adduct about 10% of the 1:2 adduct which was identified by GC-MS (see Figure 4). With CCl$_3$CF$_3$, there is also formation of a small amount of 1,1,1,4,4,4-

hexafluoro-2,2,3,3-tetrachlorobutane that can arise from dimerization of two CF$_3$CCl$_2$$^\bullet$ radicals. Thus, there is evidence of a later reaction of the 1:1 product radical with an additional alkene monomer which competes with subsequent chain transfer of the 1:1 product radical by SET and halogen transfer at a [Ni(NCN)X$_2$] site.

The exchange of the bromine atom of [Ni(NCN)Br], **1**, with chlorine atoms of carbon tetrachloride (*vide supra*) prompted us to study cross-over experiments between CBr$_4$ and CCl$_4$ in the absence and presence of MMA. In the first series of experiments, CCl$_4$ and CBr$_4$ were mixed and addition of **1** afforded three new compounds which were identified by GC-MS as CBrCl$_3$, CBr$_2$Cl$_2$ and CBr$_3$Cl. No dimeric products such as hexachloroethane or hexabromoethane, which could arise from the recombination of Cl$_3$C$^\bullet$ or Br$_3$C$^\bullet$ radicals, were detected. No exchange of halide was observed in control experiments in which **1** was not present in a solution of CCl$_4$ and CBr$_4$. Thus, the arylnickel complex is essential for the observed halogen exchange. In the second series of cross-over experiments, MMA was treated with a mixture of CCl$_4$ and CBr$_4$ in the presence of **1**. In this reaction mixture, CBr$_4$ is consumed much faster than CCl$_4$. Analysis of the reaction mixture with GLC and GC-MS showed that eight new compounds, all 1:1 adducts, had been formed (see Figure 5). The formation of these different products can be easily explained on the basis of the cross products from CCl$_4$ and CBr$_4$ that are present in the reaction mixture. Moreover, in separate experiments, we found that halogen exchange between the 1:1 adducts and excess CCl$_4$ can occur under the influence of **1**. This shows that under the standard conditions of the Kharasch addition reaction, the 1:1 adduct can be considered as a dormant species for which activation of its C−X bond is less likely than that for CCl$_4$.

Modification of the Aryldiamine Ligand System. An important aspect of the catalyst system based on aryldiamine metal complexes, such as **1**−**5**, is that the ligands offer, through modification and substitution, the ability to influence the reactivity of the complexed metal center (see Figure 1). Possible modifications include (i) changing the anion X,[10,11,15a,25] (ii) substituting the methyl groups on the N-donor atoms for other organic groups (*e.g.,* Et, *i*-Pr, *t*-Bu),[11,15b] and (iii) placing substituents on the aryl ring of the ligand system *para* to the metal center.[16] The first two modifications have already been investigated in our laboratory, and both have a marked effect on the catalytic activity of the resulting arylnickel(II) complexes.[11] The essential role of the anion X in the present catalytic system having
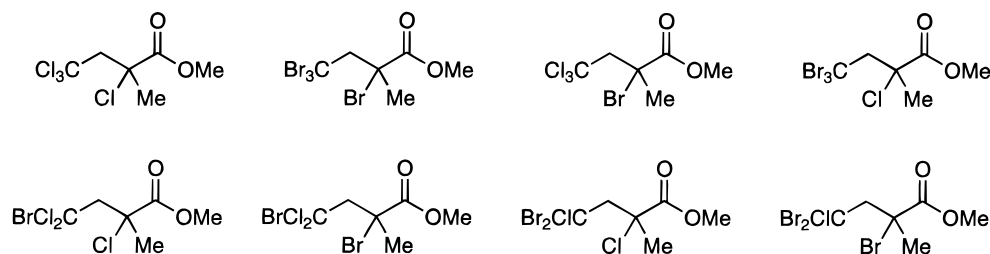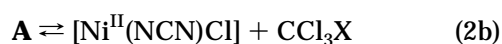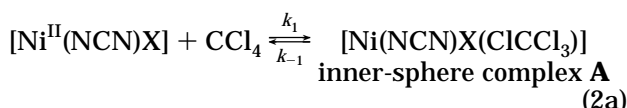
Figure 5. Products (1:1 Kharasch addition) from the cross-over experiment with MMA in the presence of CCl_4 and CBr_4. Reaction conditions: MMA (3 mL), [Ni(NCN)Br] (30 mg, 9.1×10^{-5} mol), CBr_4 (16.8 g, 51 mmol), CCl_4 (5 mL, 52 mmol), CH_2Cl_2 (12.5 mL).

been dramatically illustrated by the fact that when X is a halide (Cl, Br or I) the metal complexes do display catalytic activity. However, the ionic species [Ni-{$C_6H_3(CH_2NMe_2)_2$-2,6}(CH_3CN)]BF_4 does not exhibit any catalytic activity whatsoever. The latter result is noteworthy and provides indirect evidence that within the catalytic system being studied, Ni−X dissociation to form a cationic nickel species does not appear to afford a catalytically active species, even though an "open" coordination site is available. The bulk of the substituents on the N-donor atoms also have a pronounced effect on the reactivity of the nickel(II) complexes [Ni{$C_6H_3(CH_2NR'R'')_2$-2,6}Br]. Contrary to what could be expected from electron donor properties, the activity decreases considerably in the following order: Me > Et > *i*-Pr > *t*-Bu, *i.e.*, it decreases with increasing steric bulk at the N-donor atom.[11] This observation corroborates with the view that the initial process is comprised of the formation of an inner-sphere activated complex between [Ni(NCN)X] and the polyhalogenated alkane (eq 2). Increased steric congestion at the N-

$$[Ni^{II}(NCN)X] + CCl_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ni(NCN)X(ClCCl_3)]$$
$$\text{inner-sphere complex } \mathbf{A} \quad (2a)$$

$$\mathbf{A} \rightleftharpoons [Ni^{II}(NCN)Cl] + CCl_3X \quad (2b)$$

donor atoms will increasingly interfere with the formation of an inner-sphere complex. The same argument applies to the encounter of the 1:1 polyhalogenated alkane addition product $Cl_3CCH_2C(Cl)HMeCOOMe$, instead of CCl_4, with a Ni(II) center. Note also that the sensitivity of the cone angle to the steric bulk of the substituents is much more pronounced for tertiary amines (N-donors) than for tertiary phosphines (P-donors) since the covalent radius of nitrogen is smaller than that of phosphorus.[15b] The third modification involving the introduction of substituents (R) with either electron-donating or electron-withdrawing character at the *para*-position of the aryl ring, which should thereby directly influence the electronic properties of the C_{ipso}−Ni bond and the metal center, is also investigated in this mechanistic study.

The arylnickel(II) complexes [Ni{$C_6H_2(CH_2NMe_2)_2$-2,6-R-4}Br] (R = H (**1**), MeC(O) (**2**), Cl (**3**), MeO (**4**), NH_2 (**5**)), see Figure 1, were synthesized[16] and their catalytic ability in the addition reaction was tested. The results of these experiments show that compared to **1** (R = H), electron-withdrawing groups retard the reaction rate while electron-donating groups enhance the reaction rate. The effects of the *para*-substituents on the catalytic activity (as the relative reaction rate constant)

correlate well with the Hammett substituent constants σ_p. The negative slope ($\rho = -1.6$) indicates that there is an electron demand just before or in the rate-determining step. Previously, we showed that substituents in the *para*-position of the aryl ring influence the electronic properties of the arylnickel(II) complexes, and redox properties of the various complexes were quantified by cyclic voltammetry in dichloromethane or acetone solutions.[16] A plot of the oxidation potential of **1−5** from these earlier studies vs the corresponding catalytic reaction rate constant determined here shows a reasonable correlation (see Supporting Information). Since the oxidation of **1−5** is a one-electron transfer process (to afford a Ni(III) center), this correlation we have now identified indicates that *just before or in the rate-determing step of the catalytic cycle a one-electron oxidation probably occurs.*

Discussion

All evidence in this study of the Kharasch addition reaction points to a central role for the aryldiamine nickel halide complex in the catalytic cycle. An earlier piece of evidence that corroborates this conclusion is the fact that the steric bulk of the nitrogen donor substituents, which can influence the approach of substrates and reagents to the metal center, does indeed affect the catalytic rate.[11]

Careful consideration of all the collected data of the present and earlier studies[10,11,15a−c,16,25] allows one to propose a catalytic cycle that is not only consistent with the experimental evidence but which also provides insight into the relationship between Kharasch addition and living radical polymerization reactions that are catalyzed by the Ni(II) complexes **1−5**. In the following section, we present our proposal for the [Ni(NCN)X]-catalyzed Kharasch addition reaction. A key feature of this is a reversible activation/deactivation of the polyhalogenated alkane by concomitant SET and halide transfer in the [Ni(NCN)X] coordination sphere. This proposal has also been used to explain the controlled radical polymerization of MMA by these complexes.[7h]

Proposed Catalytic Cycle. The proposed catalytic cycle is outlined in Figure 6 with a terminal alkene $H_2C=CRR'$ as the substrate, carbon tetrachloride as the polyhalogenated alkane, and an arylnickel(II) complex [Ni(NCN)X] as the catalyst. The proposed mechanism consists of three steps. The first step involves the catalyst and CCl_4; note that the CCl_4:Ni ratio is greater than 1000:1, whereas in controlled radical polymerization the polyhalogenated alkane:Ni ratio is lower than 5:1.[7h] In this step, the reversible activation/deactivation of CCl_4 occurs. The Ni−X moiety of the catalyst is the
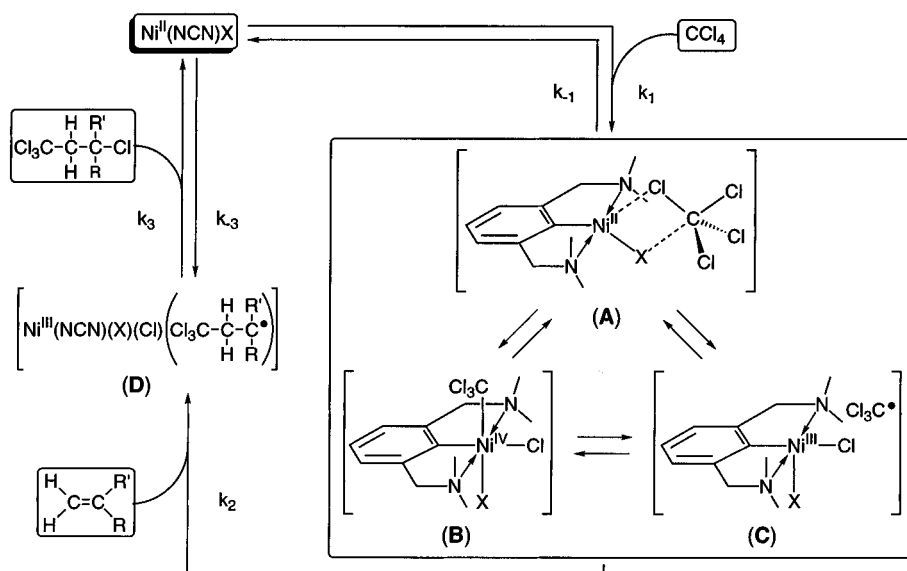
Figure 6. The postulated catalytic cycle for the Kharasch addition reaction of polyhalogenated alkanes (CCl$_4$) to alkenes in the presence of [Ni(NCN)X], **1**.

anchoring site for the formation of an inner-sphere activated complex (**A**). It is in this complex that possible SET/halogen transfer can occur, together with the generation of the Cl$_3$C• radical, *i.e.*, formation of a 1:1 Ni(III):Cl$_3$C• radical adduct (see below). In the second step, the alkene is introduced. The third stage is equivalent to the initiation steps and again involves reversible SET/halogen transfer, followed by product elimination and re-generation of the [Ni^{II}(NCN)X] complex.

The second step is the rate-determining one, in agreement with the observed first-order dependence in MMA. Consequently, the first step is a rapid equilibrium in which the catalyst [Ni(NCN)X] is likely to be predominately in the form of the inner-sphere complex due to a very large excess of the polyhalogenated alkane. The first-order in catalyst and the saturation-kinetic behavior of CCl$_4$ are in line with this conclusion.

As a product of the first step, we consider formation of the species **B** and **C** from the inner-sphere activated complex. Species **B** is an octahedral Ni(IV) intermediate that arises from a formal oxidative addition of the polyhalogenated alkane to the Ni(II) center. The other species, **C**, is a Ni(III) intermediate, [Ni^{III}(NCN)(X)Cl] with an associated Cl$_3$C• radical, *i.e.,* a complexed radical adduct, which is generated by SET to the activated alkane, followed by halide transfer. Within the coordination sphere of **C**, there are several ways of stabilizing a Cl$_3$C• radical, such as by interactions with the nucleophilic ligand sites of the halide anion or the π-system of the aryl ring. Species **B** and **C** are directly interrelated in that homolytic bond cleavage of the Ni^{IV}–CCl$_3$ unit in **B** would provide a d^7 complex with a Cl$_3$C• radical, *i.e.*, **C**.

Our kinetic results allow no discrimination between **B** and **C**. We believe, however, that the latter is the more appropriate species for describing and understanding the ensuing (Kharasch and living radical polymerization) chemistry at the metal center. One reason for such a preference is that our experimental data suggests that radical species are involved, although these species are not free radicals. Another reason is based on our electrochemical data, *i.e.*, oxidation of complexes such

as Ni(II) complexes **1**−**5** to their Ni(III) analogues is easy but further oxidation to Ni(IV) has not been achieved.[16,25b] Supporting evidence is afforded by the results obtained with both electron-donating and electron-withdrawing *para*-substituents on the aryl ring of the ligand system. We find a reasonable correlation between E_{ox} (Ni(II)/Ni(III)) of the substituted nickel complexes and their corresponding reactivity.[6] When the aryl ligand system has pyrrolidine substituents with ester functionalities, catalytic activity is lost since at this oxidation stage additional intramolecular donative O → Ni coordination stabilizes the Ni(III) state, *i.e.*, the required termination step by SET/halogen transfer to the product radical is quenched. We have previously isolated and characterized the resulting unique ionic octahedral Ni(III) complexes.[24]

In the second step, a C−C bond is formed in an inner-sphere reaction of Cl$_3$C• with the alkene. This type of association mechanism, in which steric bulk in the metal coordination sphere will influence the catalytic rate, is fully consistent with earlier experimental results with bulkier aryldiamine ligands.[15c] The rate-determining step leads to intermediate **D**, a species about which we have no experimental information (as is the case for **B**/**C**). It is clear that in the final stage of the catalytic cycle there has to be rapid SET and transfer of halide between the d^7 Ni(III) halide moiety and the adduct radical. The organic product is eliminated from the coordination sphere with regeneration of the [Ni(NCN)X] catalyst. Although in practice in the first cycle it is [Ni(NCN)Br] that is the active complex, it will be evident that as soon as the Br atom has become incorporated into the 1:1 Kharasch addition product that [Ni(NCN)Cl] becomes the catalyst for all remaining cycles.

It is worthwhile to note that step 3 is formally similar to the reverse of step 1 and that the radical in **D** is comparable to the Cl$_3$C• radical in **C**. In principle, the radical in **D** could add to a second alkene molecule. As shown above in our CCl$_4$/MMA system, the kinetics are such that the 1:1 adduct is formed exclusively, but with CCl$_3$CF$_3$ some 1:2 adduct (Figure 4) is isolated. This indicates that slower kinetics for 1:1 adduct formation

are playing a role with this substrate. Moreover, the 1:1 product $Cl_3CCH_2C(Cl)RR'$ is a polyhalogenated alkane like CCl_4 and therefore, a potential substrate for activation by [Ni(NCN)X]. Such a subsequent reaction would lead to a 2:1 adduct, but this organic product has not been detected.

Consequences of the Postulated Catalytic Cycle. Any catalytic cycle in which intermediates have radical character brings with it the question of whether free organic radical processes are also operative, particularly in a case such as this where the radicals involved are themselves quite stable (the CCl_3 radical is, for example, *ca.* 42 kJ mol^{-1} more stable than the CH_3 radical). As already stated, the first-order dependence of the catalytic rate on [Ni(NCN)X] concentration is evidence that this is not so, as is our observed reactivity sequence of $CBrCl_3 > CBr_4 > CCl_4$ which does not agree with the literature sequence[1h] for a free radical type of mechanism, *viz.* $CBr_4 > CBrCl_3 > CCl_4$. The radicals that are involved react much faster within their complex (SET/halogen transfer) than outside, except for those in the slower reactions with cyclohexene and CCl_3CF_3. The rate constant of adduct formation with cyclohexene ($k = 0.04 \times 10^{-5}$ s^{-1}) is three orders of magnitude lower than with MMA. Thus, one does see products arising from a free radical process, *i.e.*, allyl proton abstraction from cyclohexene by $Cl_3C^{\bullet}$, that is consistent with some release of this radical to the bulk solution.

There are a number of aspects worth briefly commenting on with respect to the relationship of our catalytic system to other results in this general area. The fact that the [Ni^{II}(NCN)X]/MMA/(excess) CCl_4 system solely affords the 1:1 Kharasch product is a direct consequence of the concentration of the reagents and the special ligand environment present, whereas systems like [Ni^0(CO)$_2$(PPh$_3$)$_2$]/MMA/CCl$_4$[17a] and related Ni(II) systems[7i,l] solely afford MMA polymerization. Another interesting aspect is that in our system we find saturation kinetics for the rate dependence on CCl_4 concentration and a first-order dependence in alkene. In contrast, however, in the [RuCl$_2$(PPh$_3$)$_3$] catalytic system studied by Matsumoto *et al.*[8a-e] and Davis *et al.*,[8g] there is a first-order dependence in CCl_4 and saturation[8g,26] kinetic rate dependence of the alkene. This latter aspect leads them to introduce a reversible step involving alkene coordination. This ruthenium and the related Pd(OAc)$_2$−PPh$_3$ system[41] are reported to be among the most active catalytic systems for the Kharasch addition reaction. Our catalytic system is at least as reactive as these systems, and our system effectively operates at ambient temperature under mild reaction conditions.

Two characteristic differences between our monoanionic ligand system and the commonly used neutral phosphine and amine ligands are (i) the well-defined organometallic coordination sphere is not easily disrupted owing to the combination of a Ni−C σ-bond with two chelate rings (the M−C bond of the Ni catalyst is not involved at any stage in the reaction profile and appears to be 'protected' by the chelation of the CH_2-NMe$_2$ ligand arms) and (ii) it is suitable for a number of modifications. We have, using this latter characteristic, not only successfully anchored catalytically active

Scheme 3
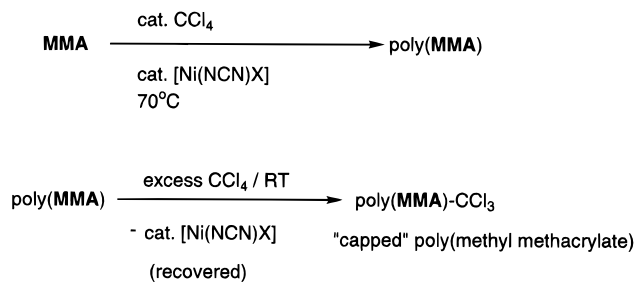
[Ni(NCN)X] sites to soluble polymers[12a] but have also prepared the first catalytically active carbosilane dendrimers.[13] This is an important aspect in terms of applications of this technology in a 'heterogeneous' (*i.e.*, industrial) sense. Of further relevance is the unique opportunities that can be envisioned using this [Ni-(NCN)X]/CCl$_4$ catalyst system. Selective system modification involving the temperature and reagent concentrations (Scheme 3) could be used to switch the catalytic behavior of the Ni complex *in situ* from polymerization to 1:1 Kharasch addition. This would lead to immediate termination of the living radical polymerization by a Kharasch 'capping' reaction (assuming kinetic control of the reaction according to $k_{Kharasch} \gg k_{polymerization}$ if [CCl$_4$] $\gg$ [catalyst] at ambient temperature). A further beneficial result of this is that it would allow for facile recovery of the catalyst from the polymer matrix (since it is released from the polymer terminus) with concomitant introduction of useful halide substituents onto the end groups of the polymer chain (Scheme 3). We are currently exploring this possibility.

A final point worth emphasizing is that in the first step of the catalytic cycle, activation of CCl_4, occurs in the absence of a free coordination site.[27-30] This is a previously unrecognized concept in homogeneous catalysis that could be of fundamental significance in systems that comprise elementary steps involving SET and metal species with an odd number of electrons.

Experimental Section

General. All reagents, except the arylnickel(II) complexes, were commercially available and used after appropriate purification. The alkenes were successively washed with 5% aqueous NaOH solution to remove inhibitors, washed twice with water, dried over MgSO$_4$, filtered, and distilled under a nitrogen atmosphere. They were stored in the dark under a nitrogen atmosphere at −30 °C. The polyhalogenated alkanes were dried over MgSO$_4$, filtered, and distilled, except for carbon tetrabromide, which was recrystallized from ethanol. Solvents were dried and freshly distilled under a nitrogen atmosphere before use. The arylnickel(II) complexes were synthesized according to literature procedures.[16] All manipulations of air-

(26) The authors[8g] prefer to use the term Michaelis−Menten to describe the rate dependence on alkene concentration.

(27) Preliminary molecular modeling studies (MM2 and ZINDO as implemented in CAChe Scientific software; Oxford Molecular Group) show that such an encounter species (**A**, Figure 6) is a viable intermediate, see: Grove, D. M. Unpublished results.

(28) For examples of isolated transition metal complexes that contain halogenated alkanes bound through halide−metal interactions, see: (a) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89 and references given therein. (b) Peng, T.-S.; Winter, C. H.; Gladysz, J. A. *Inorg. Chem.* **1994**, *33*, 2534. (c) Pathak, D. D.; Adams, H.; White, C. *J. Chem. Soc., Chem. Commun.* **1994**, 733.

(29) van der Zeijden, A. A. H.; van Koten, G.; Wouters, J. M. A.; Wijsmuller, W. F. A.; Grove, D. M. *J. Am. Chem. Soc.* **1988**, *110*, 5354.

(30) van Beek, J. A. M.; van Koten, G.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5010.

sensitive nickel complexes and all catalytic experiments were carried out under a nitrogen atmosphere using Schlenk techniques.

GLC analyses were performed on a Varian 3400 gas chromatograph equipped with a FID and an internal integrator (column, CP Sil5 (0.31 mm × 30 m); injector temperature, 250 °C; detector temperature, 250 °C; temperature program, 105 °C, 3 min, 20 °C min^{-1}, 245 °C, 5 min) and on a Varian 3700 gas chromatograph equipped with a FID and a Shimadzu C-R3A Chromatopac integrator (column, 10% Carbowax 20 M on Chromosorb W, HP 80/100 mesh; injector temperature, 250 °C; detector temperature, 250 °C; temperature program, 65 °C, 2 min, 25 °C min^{-1}, 180 °C, 3 min). Reaction products were identified by GC-MS, NMR, and GLC and also by comparison with authentic samples.

ESR spectra were recorded in CH_2Cl_2 on a JEOL RE 2X ESR spectrometer at −196 °C at the Department of Inorganic Chemistry, University of Leiden, under the supervision of Prof. Dr. J. Reedijk. UV−vis spectra were measured on Varian Cary 1 and Varian Cary 5 spectrophotometers. Infrared spectra were measured on a Perkin-Elmer FT-IR 1800 (double beam) spectrometer. Gas−liquid chromatography−mass spectrometry was carried out using a JEOL JMS-AX505W spectrometer fitted with a Hewlett-Packard 5890 gas chromatograph (CP Sil5 column (0.32 mm × 25 m)). Mass spectra, obtained under electron ionization conditions (70 eV), were recorded by linear scanning from *m/z* 35−800 at an accelerating voltage of 3 kV. Both FT-IR and GC-MS measurements were performed at the Department of Analytical Molecular Spectrometry, Utrecht University.

Standard Catalytic System. Prior to use, a mixture of methyl methacrylate (3 mL, 28 mmol) and CCl_4 (10 mL, 104 mmol) in CH_2Cl_2 (12 mL) was degassed three times using the freeze−pump−thaw method. The catalyst (9.1×10^{-5} mol) was dissolved in CH_2Cl_2 (0.5 mL) and subsequently added through a septum to the solution of alkene and CCl_4 in CH_2-Cl$_2$. The reaction mixture was kept at 25.0 ± 0.2 °C. The reaction was monitored by withdrawing samples at regular time intervals from the reaction mixture and analyzing them by GLC; dodecane was used as an internal standard.

Kinetic Studies. The kinetic experiments were performed in a manner similar to that described for the standard catalytic system. To determine the orders in the various reagents, the concentrations of the catalyst, CCl_4, and alkene were varied during independent series of experiments. The total volume of the solution was maintained at 25.5 mL by adding sufficient CH_2Cl_2.

The activation parameters were determined by variation of the reaction temperature. The various temperatures were held constant by a constant temperature bath (Tamson NV, Holland, and Frigomix B. Braun, Melsungen).

Supporting Information Available: Graphs of the first-order dependence of the reaction rate (k) vs catalyst (Ni[NCN]-Br) concentration, CH_3CN concentration, and MMA concentration, the log (k/k_o) vs Hammett substituent parameters (σ_p) for the addition of CCl_4 to MMA by complexes **1**−**5**, and correlation of the oxidation potential $E_{p,a}$ vs log(k/k_o) for complexes **1**−**5** (5 pages). Ordering information is given on any current masthead page.