Chapter 5

# Selective Product Formation with Organometallic Radicals of Nickel and Zinc

**Gerard van Koten, Robert A. Gossage, David M. Grove, and Johann T. B. H. Jastzebski**

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

A summary is presented of the mechanistic study of the 1 : 1 Kharasch addition reaction of polyhalogenated alkanes to olefins catalyzed by mononuclear or dendrimer-bound aryl-Ni complexes. These compounds contain the terdentate monoanionic aryldiamino ligand, $[C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}R\text{-}4]^-$ or "(NCN)". The catalysis occurs *via* inner sphere single electron transfer (SET) with the formation of a $Ni^{III}$ organometallic radical and a polyhalogenated alkane radical. This study is also relevant to the use of such compounds for the controlled radical polymerization of alkenes. A review is also given of the chemistry of α-diimine containing organozinc radicals that are also formed by a SET process. These metal-based radicals are useful for a variety of highly selective group transfer reactions in organic synthesis.

Moses Gomberg was the first to isolate an organic radical, the triphenylmethyl radical, almost 100 years ago (*1*). It is unlikely that he could have forseen the important role that such organic and organometallic radicals play in modern synthetic chemistry. Radicals are key intermediates in many important chemical processes including addition, polymerization and group transfer reactions. Research in our group has been aimed at controlling these reactions by the use of isolable, paramagnetic (*i.e.* radical) organometallic complexes.

## Homogeneous Catalysis with Organonickel Complexes; Reactions and Mechanism.

**Catalysis.** We have designed and synthesized a vast array of main-group and transition metal complexes of the general structure **1** (Figure 1) incorporating the monoanionic diaminoaryl ligand $[C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}R\text{-}4]^-$, abbreviated as "(NCN)".(*2, 3*) This organic fragment generally enforces a rigid trans disposition of the N donor atoms in relation to the metal-aryl group, an arrangment which

generally constrains an overall meridonal geometry around the metal centre (*2,3*). $NiX_n(NCN)$ complexes have been isolated for the formally $Ni^{II}$ (X = halide; n = 1) and $Ni^{III}$ (X = halide; n = 2) oxidation states (Figure 1). The trivalent compounds were the first organometallic $Ni^{III}$ compounds to be isolated and structurally characterized (*2-4*). It has been shown that when $[Ni^{II}(NCN)]$ complexes are used as pre-catalysts, that the active species (discussed below) is a highly active promoter not only for addition reactions but also in the controlled radical polymerization of alkenes. The mononuclear Ni complex **1a** is an excellent homogeneous catalyst for the 1 : 1 Kharasch addition reaction of halocarbons to olefins *via* an inner sphere electron transfer process (also referred to as "atom transfer", see Scheme 1), when a large excess of halocarbon is used. This reaction occurs readily at ambient temperature and pressure (*5*).

Kharasch addition is important in specialty chemical synthesis, as the trichloromethyl group can be readily converted into a variety of useful functional groups (*6*). We have carried out an extensive investigation of the factors that control this process (*i.e.* catalytic 1 : 1 Kharasch addition) and by so doing have identified that during catalysis a paramagnetic, $d^7$, Ni(III) organometallic complex (*i.e.*, a radical) is formed.

**Mechanistic Studies of Nickel-Catalyzed Kharasch Addition.** We have carried out a detailed study of the catalytic mechanism using [NiX(NCN)] as catalyst. The systematic adjustment of the ligand environment and reaction conditions during catalysis was carried out by: (i) varying the ligand X bound to Ni (*5*), (ii) varying the R group on the para-position of the (NCN) ligand (Figure 1) (*8*), (iii) substitution of the methyl groups attached to nitrogen by bulkier and more electron rich fragments (*5, 6, 9, 10*) and (iv) adjustment of the reagents (catalyst, alkene and polyhalogenated alkane) used and their concentrations under controlled catalytic conditions.

**Early Work.** Early experiments had indicated that the type of the halide anion (Cl, Br or I) coordinated to Ni had little effect on the overall reaction profile for the catalytic Kharasch (*i.e.* 1 : 1) addition of $CCl_4$ to methyl methacrylate (MMA) or other alkenes (*4*). Replacement of this halide by a neutral donor ligand results in the formation of a $Ni^{II}$ cation as the catalyst precursor, such as the complex $[Ni(NCN)(MeCN)]BF_4$ (*4, 5*). These cationic species are completely *inactive* as catalysts for the Kharasch addition reaction, a result which clearly demonstrates the necessity of a halide ligand in the catalytic cycle and *not* the availability of an open coordination site(s).

**Ligand Modification.** The effect of replacing the proton as the R group on the para position of the (NCN) ligand was also investigated. Catalytic reaction rates were found to increase with electron donating substituents while electron withdrawing groups have the opposite effect. A linear relationship was found between the Hammett (substituent) parameters of the R group and the reaction rate. This result indicates that there is an electron demand at or just before the rate determining step. It was also observed that this modification of the rate of catalysis could be directly related to the value of the $Ni^{II}$ / $Ni^{III}$ redox couple. This suggests that oxidation of the metal is an essential part of the catalysis and that $Ni^{III}$ complexes are probably formed (*8,11*).

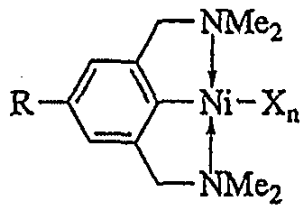
The increase in the catalytic rate as a result of the introduction of electron donating R groups led us to investigate if this effect could be further enhanced by the replacement of the methyl groups attached to nitrogen. Modified (NCN) ligands incorporating electron-rich (*e.g.* isopropyl) groups were used to synthesize the corresponding $Ni^{II}$ catalyst precursors. These complexes have greatly *reduced* (or no) catalytic behaviour. The effect seems to be steric in nature and indicates that the $NMe_2$ groups are a necessary component of this catalytic system. This also provides evidence that the initial process involves the formation of an innersphere activated complex between [NiX(NCN)] and the polyhalogenated alkane. Increased steric congestion at the N donor atoms will interfere with the production of this complex and hence the reaction rate will be retarded.

**Concentration Effects on Catalysis.** Catalytic studies have also been performed using different concentrations of catalyst, alkene and halocarbon. The rate law is distinctly first order in relation to catalyst and alkene concentration. This indicates that the activated complex is a mononuclear one and that alkene activation is rate determining. Varying the concentration of the polyhalogenated alkane shows that the reaction rate has a dependence that is typical of *saturation kinetics*. The inference here is that the reaction of this alkane with the Ni complex is *reversible*. Furthermore, cross-over experiments with mixtures of $CCl_4$ and $CBr_4$ indicate that an equilibrium, such as that shown in Scheme 2, is probably operating (*i.e.* in step 1, $k_1$ and $k_{-1}$ are reversible and "X" can be readily exchanged for a halide atom from $CCl_4$ or $CBr_4$).

**Spectroscopic Studies During Catalysis.** Spectroscopic studies (IR, NMR) of the catalytic and stoichiometric reaction of [NiBr(NCN)] with MMA revealed no evidence for $\eta^2$-coordination of the olefinic C=C bond to the metal centre. Measurements by ESR spectroscopy taken during catalysis confirm the formation of a $Ni^{III}$ complex of very similar structure to that of the previously isolated [$NiX_2$(NCN)] compounds (*4, 11*).

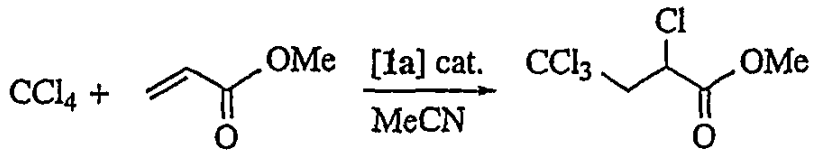
These data suggest the presence of radicals, similar to those that have been proposed in the mechanism of Kharasch addition mediated by inorganic halides and $RuCl_2(PPh_3)_3$ (*12, 13*). Two main factors also point to the production of radicals in the coordination sphere of the metal. First, none of the reaction products that have been detected are consistent with the bulk release of free radicals into the reaction medium under the conditions of study, *e.g.*, the formation of hexachloroethane from the addition reaction of two free $^{\bullet}CCl_3$ radicals. Secondly, the observation of $Ni^{III}$ radical complexes indicates directly that inner sphere single electron transfer (SET) has occurred from the interaction of the $Ni^{II}$ pre-catalyst and the polyhalogenated alkane.

**Proposed Mechanism.** Based on all of the above observations, we have proposed a catalytic cycle (see Scheme 2) based on a non-chain mechanism with a mononuclear Ni species. During or just prior to the rate determining step, oxidation of the $Ni^{II}$ metal centre to a $d^7$ $Ni^{III}$ organometallic radical occurs *via* SET (complex **C**, Scheme 2; *c.f.*, **B** represents the possible case of oxidative addition of $CCl_4$ to the Ni center). This step leads to the generation of both a [$NiX_2$(NCN)] centre and a polyhalogenated organic radical in the coordination sphere of the metal atom where it reacts, in the rate determining step, with the alkene. Following this,

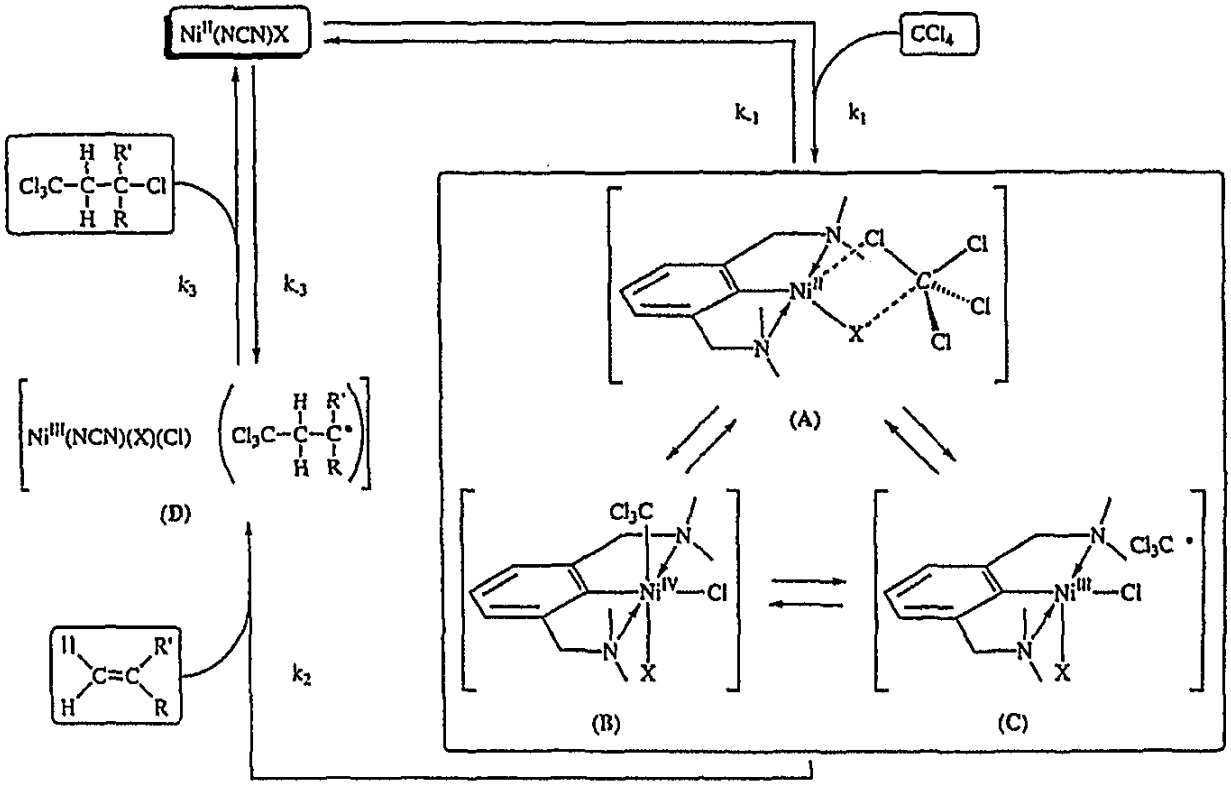



**1a**

Figure 1.




Scheme 1.




Scheme 2. The proposed mechanism of the 1 : 1 Kharasch addition reaction of polyhalogenated alkanes to olefins.

rapid halide transfer (atom transfer) is mediated by the $Ni^{III}$ halide moiety to the adduct radical. The 1 : 1 addition product is then eliminated from the vicinity of the metal with regeneration of the [NiX(NCN)] complex, see Scheme 2 (*11*). We believe that the organic radicals that are involved in this chemistry remain in the coordination sphere of the metal complex. This is suggested by the reaction profile and the products thus formed, *vide supra* (*7, 11, 12*). An interesting feature of this system is the role of the Ni-X fragment as an anchoring site for the formation of an innersphere activated complex A in the absence of a free coordination site. 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 (*i.e.* radicals).

**Other Catalytic Applications (Controlled Radical Polymerization).** A common feature of all metal-based Kharasch addition catalysts is a low inherit redox couple. For example the $Ru^{II}$ / $Ru^{III}$ and $Cu^{I}$ / $Cu^{II}$ redox couples are -0.08 and approximately +0.16 V respectively for $RuCl_2(PPh_3)_3$ and Cu halide systems (*12, 13*). Our [NiX(NCN)] complexes have an average redox couple of about +0.20 V (*2, 8-10*). Typical values for the $Ni^{II}$ / $Ni^{III}$ redox couple are on the order of +0.70 to +1.2 V (*14*). An interesting recent observation by Teyssié and coworkers is that complexes which possess this low oxidation potential can be tuned to perform polymerization reactions by adjusting the conditions. This switch of reactivity occurs at elevated temperatures in the presence of a large excess of alkene if the polyhalogenated alkane (*e.g.*, $CCl_4$) is used in *stoichiometric* amounts relative to the catalyst (*15*). Teyssié's group has shown that our [NiBr(NCN)] (R = H) complex combined with a slight excess of $CCl_4$ and a large (>1000 fold) excess of olefin is a highly active catalytic system for the controlled radical polymerization of MMA (*15*). This area has been the focus of pioneering studies by Matyjaszewski and collaborators who have produced polymers with very narrow polydispersities ($M_n < 1.05$) from a variety of olefins using a number of different catalysts (*16, 17*). An immediate consequence of Teyssié's work is the realization that controlled radical polymerization can be "switched" over to a 1 : 1 Kharasch polymer "capping" addition reaction. This could be performed *in situ* simply by quenching the living polymer with a large excess of polyhalogenated alkane with concurrent lowering of the reaction temperature. This implies that kinetic control of the reaction can be achieved by varying the reagent concentrations. In other words, the rate of polymerization ($k_P$) would have to be much less then the corresponding rate of Kharasch addition ($k_K$) in the presence of a large excess of halocarbon (*i.e.*, $k_P \ll k_K$ if [$CCl_4$] » [catalyst]). Teyssié's results clearly show that this reactivity is inverted if the concentration of catalyst and halocarbon are similar (*i.e.*, $k_P \gg k_K$ if [$CCl_4$] ≈ [catalyst]) and the reaction is performed above ambient temperature. A recent example of this *in situ* adjustment of catalytic reactivity has been demonstrated by Coca and Matyjaszewski. In this case a Cu halide / amine catalyst system was used to mediate the formation of block copolymers of styrene and (methyl)acrylates *via* initially living carbocationic then later living radical polymerization (*18*).

**Dendrimer Catalysts.** Following our early success with the [NiX(NCN)] series as Kharasch addition catalysts (*19*), we also wished to expand this chemistry to include macromolecules incorporating the active Ni unit. This can lead to the

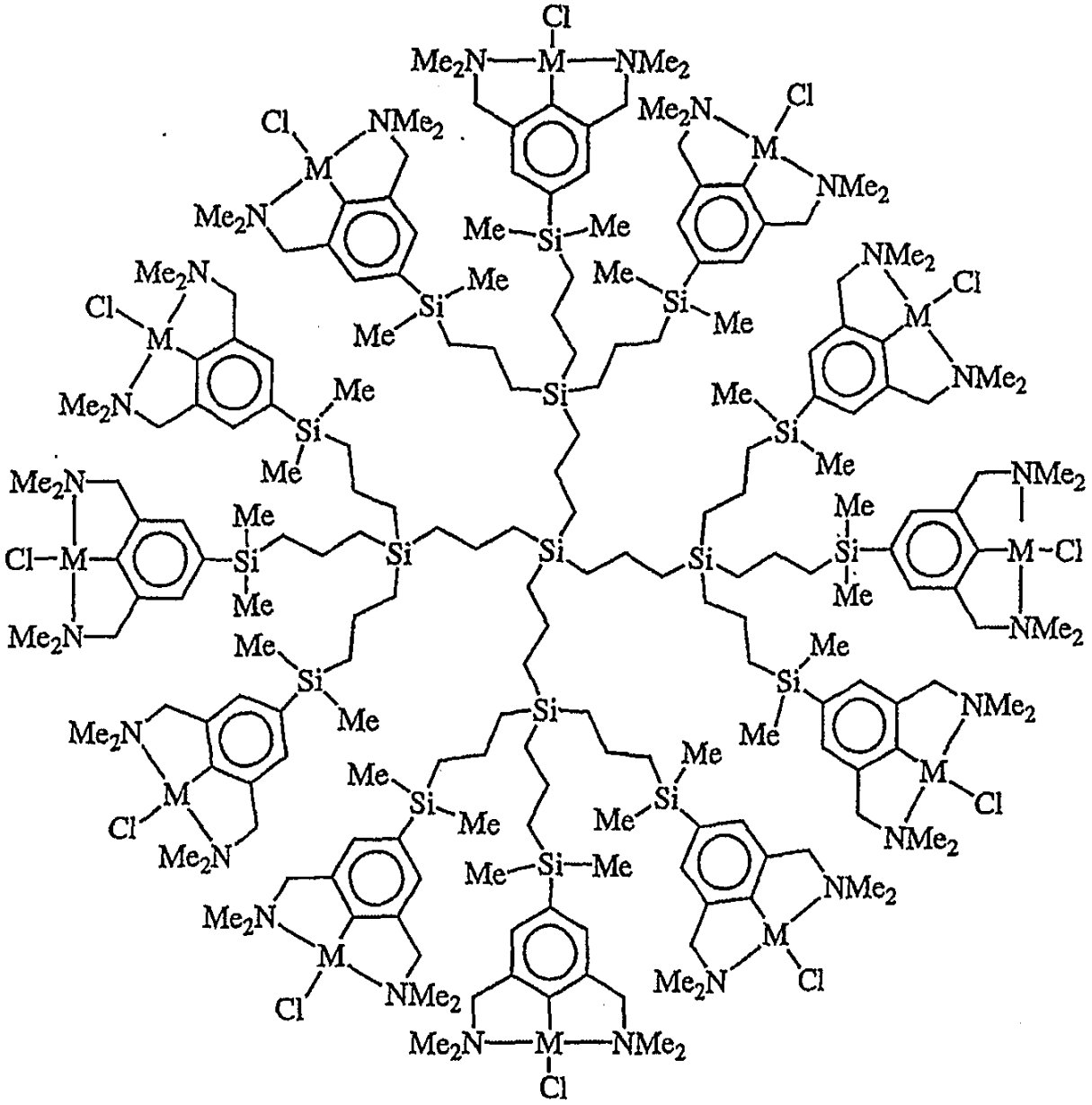



Figure 2. An example of a carbosilane dendrimer catalyst.

formation of soluble species that can be easily removed from the reaction stream by filtration or other techniques. In this regard, we designed and tested the first "dendrimer catalyst" (*20*) Dendrimers are large monodispersed molecules that are generally synthesized by a repetitive reaction sequence (*21, 22*). By using an appropriate R group attached to the (NCN) moiety (Figure 1), the grafting of the [NiX(NCN)] catalytic site on to the exterior of a carbosilane dendrimer (*23, 24*) has been achieved, see Figure 2. Catalytic activity per Ni site is maintained relative to the monomeric complex and the dendrimer unit is highly soluble in most solvents (*20, 25*) We are currently expanding these investigations to include the use of ultrafiltration technology to faciliate dendrimer (*i.e.*, catalyst) recovery from the reaction medium (*25*).

**Heterogeneous Catalysts and New Materials.** Our work on homogeneous and dendrimeric catalysis with the [NiX(NCN)] system has also been expanded to include heterogeneous catalysis. Using a similar methodology as has been shown in the dendrimer synthesis, the attachement of the Ni moiety to siloxane polymers has also been demonstrated (*26*). These polymeric materials containing the immobilized catalyst show good catalytic activity in the Kharasch addition reaction that is of the same order of magnitude as that observed with the homogeneous mononuclear complex (*26*).

Our involvement in the synthesis of new materials is not restricted to the design and use of dendrimers. We have also shown that the [NiX(NCN)] fragment is a useful starting material for the incorporation of paramagnetic (*i.e.*, radical) Ni ions into inorganic colloids (*27*). Thus, Ni(NCN) complexes have been used to produce magnetic silica particles and this presents an opportunity to study model colloidal materials that contain a covalently bound paramagnetic surface layer.

**Organozinc Radicals.**

Thus far we have described our work (and the work of others) in radical based catalysis (both homo- and heterogeneous) for selective addition and polymerization reactions. We have also shown that Ni complexes can be used to form stable paramagnetic materials. In separate studies we have also explored the use of selective group transfer reactions in organic synthesis. This chemistry involves the employment of organozinc complexes and substrates containing the α-diimine -N=CH-CH=N- skeleton. These reactions occur *via* radical pathways involving persistent organozinc α-diimine radical species. Reports on this chemistry can be found in the literature in references 28-32. Although these reactions are extremely useful for the "one-pot" synthesis of rather complex organic molecules, it is particularily the mechanistic aspects and the intermediacy of organozinc α-diimine radicals that make this chemistry interesting.

**Group Transfer Reactions.** Selective group transfer reactions can be performed with dialkylzincs containing a coordinated α-diimines R'N=CHCH=NR'. If the α-diimine used has R' = t–Bu, this reagent reacts with $ZnR_2$ with high regioselectivity to form either the nitrogen-alkylated product, ZnR(t–BuN(R)CHCHNt–Bu) (R = primary alkyl group) or the carbon-alkylated product, ZnR(t–BuNCH(R)CHNt–Bu) (R = tertiary/benzylic alkyl group) (*31*). Two possible mechanisms for this alkylation reaction have been put forward, *i.e.* a

radical and a polar mechanism, see Scheme 3. Earlier studies have shown that in both mechanisms the initial step is the formation of a thermally unstable 1:1 coordination complex $ZnR_2$(t–BuNCHCHNt–Bu) (**2**), which undergoes an intramolecular single-electron transfer (SET) reaction to give radical pair, [R• / ZnR(t–BuNCHCHNt–Bu)•] (**3**), in a solvent cage. In the radical mechanism, **3** collapses in the solvent cage, resulting in the nitrogen- (**6**) and carbon-alkylated (**7**) products. In the polar mechanism, a steady state concentration of the free organozinc radical is formed. The latter transfers its unpaired electron to the initial 1:1 coordination complex $ZnR_2$(t–BuNCHCHNt–Bu) (**2**), to give a organozinc cation / diorganozinc radical-anion pair, [ZnR(t–BuNCHCHNt–Bu)$^+$][$ZnR_2$(t–BuNCHCHNt–Bu)•$^-$] (**8**). Nucleophilic attack of an alkyl group of the diorganozinc radical-anion [$ZnR_2$(t–BuNCHCHNt–Bu)•]$^-$ on the organozinc cation [ZnR(t–BuNCHCHNt–Bu)$^+$] gives the alkylation products and simultaneous regeneration of the free organozinc radical (**4**). In the polar mechanism **6** and **7** can be regarded as 1,2- and 1,4-addition products, respectively.

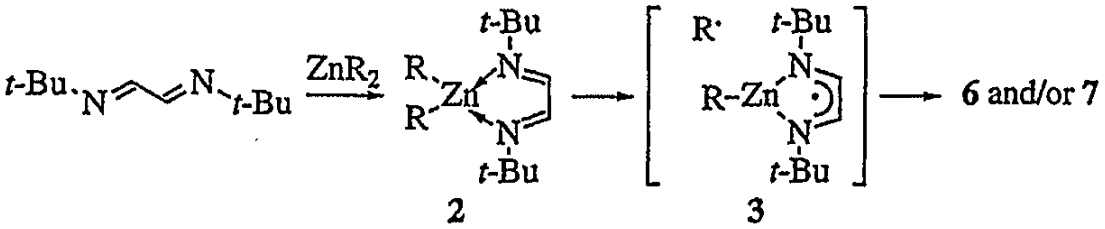
**Radical Mechanisms in Group Transfer.** Thus far, both mechanisms are supported by the isolation of the 1:1 coordination complex $ZnMe_2$(t–BuNCHCHNt–Bu) (**2a**) (*30*) and of [ZnR(t–BuNCHCHNt–Bu)]$_2$ (R = Me (**5a**), Et (**5b**)), which exist in solution in equilibrium with the corresponding neutral organozinc radicals [ZnR(t–BuNCHCHNt–Bu)] (**4**), see Scheme 4 (*28-32*). Although the radical mechanism has been used as a working hypothesis for the reaction of t–BuNCHCHNt–Bu with $ZnR_2$, the proposal of an alternative, polar mechanism seemed justified by the EPR-detection of an unprecedented paramagnetic species during the alkylation reaction in THF solution (THF = tetrahydrofuran).

Recent results provide indirect evidence for a radical mechanism in the alkylation reactions of t–BuNCHCHNt–Bu with diorganozinc compounds. The paramagnetic species detected during this alkylation reaction in THF is tentatively assigned to be the solvated neutral organozinc radical complex [ZnR(t–BuNCHCHNt–Bu)(THF)]. This conclusion is further corroborated by the observed stability of the 1:1 coordination complex **2a** toward reduction by **4a**. We have also investigated the use of the stable dimeric zinc species **5a** (and its derivatives) to generate alkylzinc(α-diimine) radicals (*e.g.*, **4a**, see Scheme 4) in the radical polymerization of alkenes.

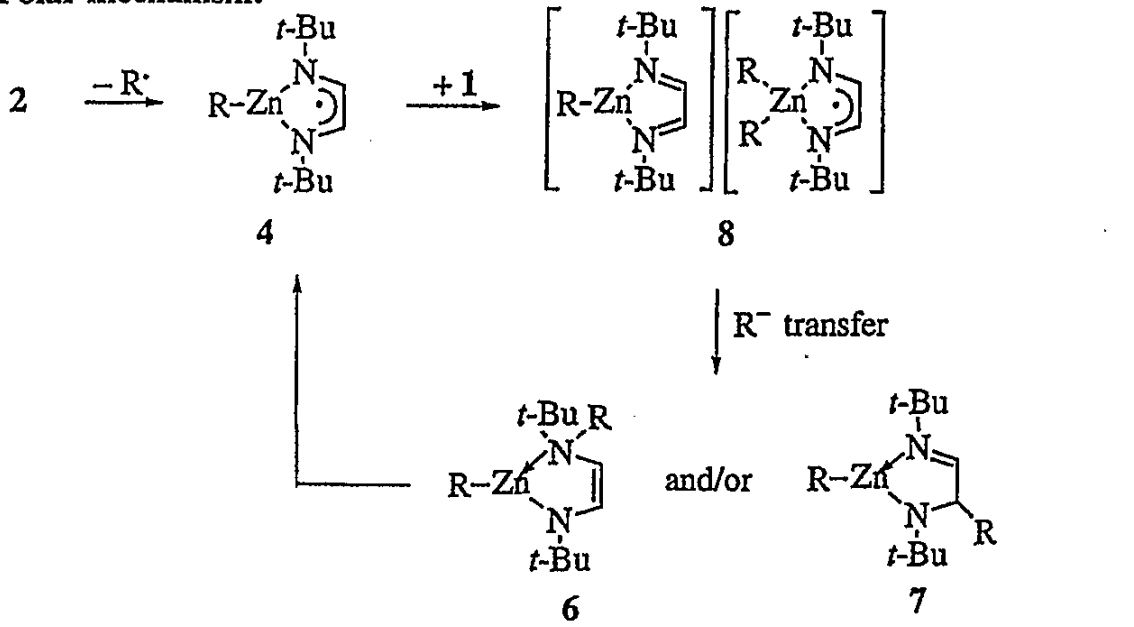
## Conclusions.

So far we have been unable to initiate polymerization with these organozinc α-diimine radicals. It should be noted that Matyjaszewski *et al* have successfully polymerized MMA with $Cu^IX$(α-diimine) compounds (α-diimine = 2,2'-bipyridine) *via* controlled living radical polymerization. The coordinated α-diimine ligand has a low lying $\pi^*$ orbital that can readily accommodate a single electron. This is also the case with our organozinc complexes (*28-32*), whereas in the case of the [$Ni^{III}X_2$(NCN)] radical the single electron resides on the metal in a HOMO directed towards the apical halide atom (*4, 9, 10*). It is this latter property that makes the [$Ni^{III}X_2$(NCN)] species a highly efficient single electron acceptor and

**Radical mechanism:**

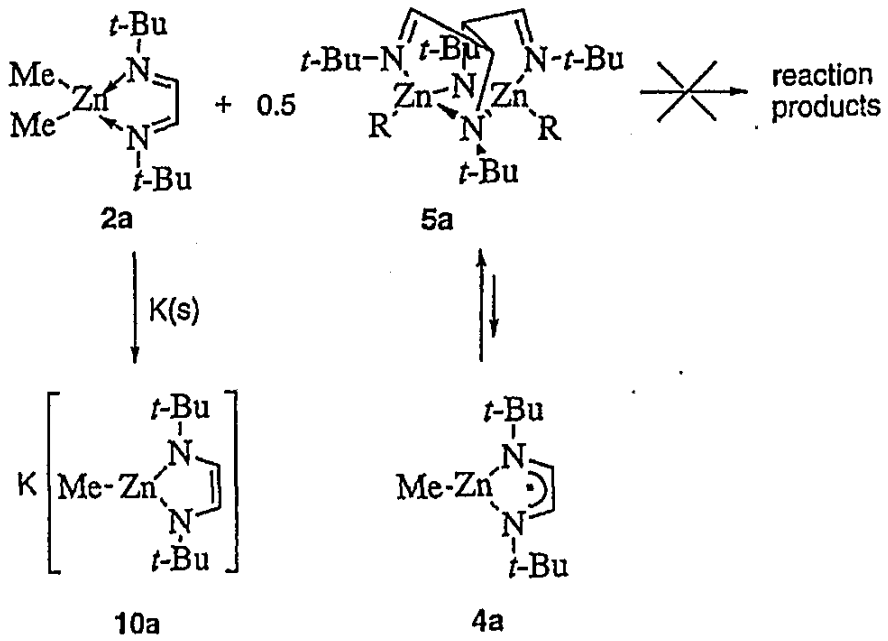



**Polar mechanism:**




R = prim. alkyl group R = tert./benzylic alkyl group

Scheme 3.




Scheme 4.

halide donor to a radical species. Thus, these characteristics make this compound both an excellent atom transfer (Kharasch addition) catalyst (*5, 6, 20, 26*) as well as an effective mediator of controlled radical polymerization (*15*).

**Acknowledgments.**

The orgaonzinc / α-diimine chemistry is part of the Ph.D. theses of Dr. E. Rijnberg and Dr. E.Wissing. We thank Dr. J. Boersma for his interest and suggestions and Dr. A. L. Spek (Utrecht University) for the crystallographic support.
This work was supported by the Netherlands Foundation for Scientific Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

**Literature Cited.**

1. Gomberg, M. *Chem. Ber.* **1900**, *33*, 3150; *J. Am. Chem. Soc.* **1900**, *22*, 757.
2. van Koten, G. *Pure & Appl. Chem.* **1989**, *61*, 1681.
3. Rietveld, M. H. P.; Grove, D. M.; van Koten, G. *New. J. Chem.* **1997**, *21*, 751.
4. Grove, D. M.; van Koten, G.; Zoet, R.; Murrall, N. W.; Welch, A. *J. Am. Chem. Soc.* **1983**, *105*, 1379.
5. Grove, D. M.; van Koten, G.; Verschuuren, A. H. M. *J. Mol. Catal.* **1988**, *45*, 189.
6. Grove, D. M.; Verschuuren, A. H. M.; van Koten, G.; van Beek, J. A. M. *J. Organomet. Chem.* **1989**, *372*, C1.
7. Bellus, D. *Pure & Appl. Chem.* **1985**, *57*, 1827.
8. 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.
9. 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-Bays* **1994**, *113*, 267.
10. 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.
11. van de Kuil, L. A.; Grove, D. M.; Gossage, R. A.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics*, in press.
12. Minisci, F. *Acc. Chem. Res.* **1975**, *8*, 165.
13. Davis, R.; Furze, J. D.; Cole-Hamilton, D. J.; Pogorzelec, P. *J. Organomet. Chem.* **1992**, *440*, 191 and references therein.
14. Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77.
15. Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1996**, *29*, 8576.
16. Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674 and references therein.
17. Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.
18. Coca, S.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 2808.
19. van de Kuil, L. A.; Grove, D. M.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *6th IUPAC Symposium on Organometallic*

*Chemistry Directed Towards Organic Synthesis*, Utrecht, The Netherlands, **1991**.

20. 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.
21. Fréchet, J. M. J. *Science* **1994**, *263*, 1710.
22. Tomalia, D. M. *Sci. American* **1995**, *272*, 62.
23. Roovers, J.; Zhou, L. L. Toporowski, P. M.; van der Zwan, M.; Iatrou, H.; Hadijchristidis, N. *Macromolecules* **1993**, *26*, 4324 and references therein.
24. van der Made, A. W.; van Leeuwen, P. W. N. M.; de Wilde, J. C.; Brandes, R. A. C. *Adv. Mater.* **1993**, *5*, 466 and references therein.
25. Kleij, A. W.; Gossage, R. A.; Kleijn, H.; van Koten, G.; Kragl, U.; Brinkmann, N. *KNCV Katalyse Symposium*, May **1997**, Kerkrade, The Netherlands, Poster 37.
26. van de Kuil, L. A.; Grove, D. M.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Chem. Mater.* **1994**, *6*, 1675.
27. Pathmamanoharan, C.; Wijkens, P.; Grove, D. M.; Philipse, A. P. *Langmuir* **1996**, *12*, 4372.
28. Klerks, J. M.; Jastrzebski, J. T. B. H.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1982**, *244*, 107.
29. van Koten, G.; de Meijere, K.; tom Dieck, H. in *Organometallics in Organic Synthesis*, Springer-Verlag, **1987**, 277.
30. Kaupp, M.; Stoll, H.; Preuss, H.; Kaim, W.; Stahl, T.; van Koten, G.; Wissing, E.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 5606.
31. Wissing, E.; Kaupp, M.; Boersma, J.; Spek, A. L.; van Koten, G. *Organometallics* **1994**, *13*, 2349.
32. Wissing, E.; van der Linden, S.; Rijnberg, E.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1994**, *13*, 2602.