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Preliminary communication

**The homogeneously catalysed addition reaction
 of polyhalogenoalkanes to olefins by divalent arylnickel
 complexes: comparative reactivity and some important
 mechanistic leads**

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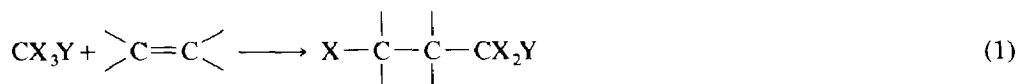
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Abstract

In comparative studies some bis(*ortho*-chelated) arylnickel compounds of the type $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NRR}')_2-2,6\}\text{X}]$ have been tested for activity in the Kharasch addition reaction of polyhalogenoalkanes to an alkene double bond using methyl methacrylate as substrate and carbon tetrachloride as reagent. The N-donor substituent combination $\text{R} = \text{R}' = \text{Me}$ produces a complex with higher reactivity than either of the combinations Et,Et, and Me,i-Pr, and the influence of the halide X is small; catalytic efficacy decreases in the order $\text{I} \sim \text{Br} > \text{Cl}$ ($\text{R} = \text{R}' = \text{Me}$). The related palladium and platinum complexes $[\text{M}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}\text{X}]$ ($\text{M} = \text{Pt}$, $\text{X} = \text{I}$; $\text{M} = \text{Pd}$, $\text{X} = \text{Br}$) show no catalytic activity in this reaction, though the complex $[\text{Pd}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMePh})_2-2,6\}\text{Br}]$ does initiate alkene polymerization. A mechanism consistent with these results is outlined.

The Kharasch addition of polyhalogenoalkanes to an alkene double bond, eq. 1,



(X = halogen; Y = H, halogen, CF_3 or other electronegative group)

is a well known reaction that can be homogeneously catalysed by various metal complexes to give the 1/1 adduct in a regiospecific manner. The CuCl catalysed reaction, in particular, is of industrial importance for the preparation of pyrethroid

insecticide precursors [1] and research into both applications and the mechanism(s) of the metal complex catalysed reaction are current [1–4].

We recently reported that the interesting organometallic nickel(II) complexes $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}\text{X}]$ ($\text{X} = \text{Cl}$, **1a**; $\text{X} = \text{Br}$, **1b**; $\text{X} = \text{I}$, **1c**) [5] containing a monoanionic terdentate N,C,N-donor ligand are exceptionally good and novel catalysts for the reaction of eq. 1 [6]. With the chloride derivative **1c** we investigated some aspects of the scope of this catalyst using methyl methacrylate and hept-1-ene as substrates with the perhaloalkanes CCl_4 , CBr_4 , and CF_3CCl_3 as reagents; the influence of the solvent on the course of the catalysed reaction was also examined. To gain further insight into the mechanism of this new system and to enable optimization of the metal complex catalyst a series of related nickel triad complexes **2–9** * have now been examined for potential catalytic activity. These studies, reported here, show the dominant role of the steric bulk of the N-donor substituents and the importance of an easily oxidizable nickel(II) centre; a mechanism consistent with the results is outlined.

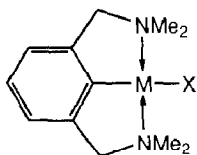
The nickel triad compounds **1–9** containing terdentate ligand aryl systems have been tested for catalytic activity in the Kharasch addition of carbon tetrachloride to methyl methacrylate; in this reaction the usual product of metal-catalysed addition is the 1/1 adduct $\text{Cl}_3\text{CCH}_2\text{CCl}(\text{Me})\text{CO}_2\text{Me}$. In our tests a small amount of acetonitrile was also added to the alkene substrate and halocarbon reagent and the two standard solutions employed had 1/10/1 and 5/20/1 volume composition of the methyl methacrylate/ CCl_4 / CH_3CN mixture. The results of this screening for potential catalytic activity, including the reaction conditions and amount of metal complex used, are gathered in Table 1.

The halide influence was investigated using $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}\text{X}]$ ($\text{X} = \text{Cl}$, Br , I ; **1a–1c**); the results obtained with an alkene-to-catalyst ratio of 702/1 are found in entries 1–9. The halide does appear to have some effect and the rate of reaction (as reflected in the percentage alkene conversion after 3 h at 20°C) decreases in the order $\text{I} \sim \text{Br} > \text{Cl}$; the chloro complex **1a** giving an initial rate that is approximately 40% lower than that for either **1b** or **1c**. The high reactivities and selectivity of the catalysis with **1a–1c** result in alkene to adduct conversions after 45 h of more than 90% in all cases, and it is the similarity of these results (rather than the absolute order of reactivity) that is of most significance. It is worth emphasising that with the catalyst concentrations employed (i.e. $< 0.003 \text{ M}$) exactly reproducible quantitative results can be difficult to obtain owing to the sensitivity of the catalytic system to oxygen **. When a reaction mixture identical to that of entry 7 (**1c** as catalyst) was aereated for 5 s after preparation it turned pale purple (a colour characteristic of Ni^{III} species with the $\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}$ ligand) and the system showed no catalytic activity. This is consistent with our earlier observation that pure $[\text{Ni}^{\text{III}}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}\text{Br}_2]$ is not catalytically active.

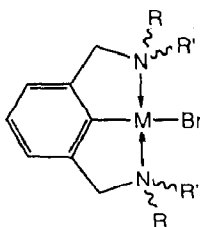
New substituents on the aryl ring of the terdentate ligand, particularly at the site

* The preparation of complexes **2–6**, **8** and **9** is fully described in forthcoming papers by Van Beek et al. Complex **7** is prepared in a manner totally analogous to that for compounds **1** [5] using an ethereal solution of $[\text{Li}\{\text{C}_6\text{H}_3(\text{OMe-4})(\text{CH}_2\text{NMe}_2)_{2-2,6}\}]$ (prepared from $\text{C}_6\text{H}_2(\text{OMe-4})(\text{Br-1})(\text{CH}_2\text{NMe}_2)_{2-2,6}$ and lithium metal) with $[\text{NiCl}_2(\text{P-n-Bu}_3)_2]$.

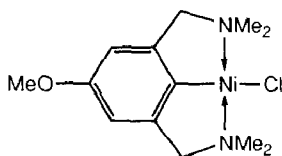
** This particular aspect may explain our original reactivity order of **1a** > **1b** > **1c** [6].



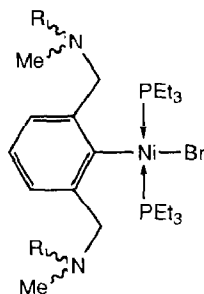
- 1a:** M = Ni, X = Cl
1b: M = Ni, X = Br
1c: M = Ni, X = I
2: M = Pd, X = Br
3: M = Pt, X = I



- 4:** M = Ni, R = R' = Et
5: M = Ni, R = Me, R' = i-Pr
6: M = Pd, R = Me, R' = Ph



7



- 8:** R = Ph
9: R = t-Bu

para to the metal centre may, through inductive or mesomeric effects, influence the electronegativity of the metal and consequently effect (either positively or negatively) the ability of the complex to affect catalysis. In a program to investigate such aspects we have prepared the new complex $[\text{Ni}\{\text{C}_6\text{H}_3(\text{OMe}-4)(\text{CH}_2\text{NMe}_2)_2-2,6\}\text{Cl}]$ (**7**) in which the presence of a mesomerically electron-donating *para*-methoxy group may make the oxidation of Ni^{II} to Ni^{III} easier than in **1** where the *para*-substituent is a H atom. The results for **7** (entries 10–12) show that although it is more active than **1a** by a factor of ~ 1.5 over the first half hour of catalysis, over longer periods it does not achieve better turnovers than complexes **1**.

To discover whether the nature of N-donor atom substituents (R,R') in $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NRR}')_2-2,6\}\text{X}]$ species affects this type of catalysis and, if so, whether the Me,Me combination in **1** is optimal, the catalytic behaviour of $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{N}(\text{Me})\text{-i-Pr})_2-2,6\}\text{Br}]$ (**4**) * and $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NEt}_2)_2-2,6\}\text{Br}]$ (**5**) was compared with that of **1**. Contrary to our expectations, based on the electronic effects of Me, i-Pr and Et groups, it is found (entries 13 and 14) that the Me,i-Pr and Et,Et combinations both afford complexes with considerably reduced catalytic activity. Not only is the reactivity of **4** and **5** comparatively low even at 65°C , but the specificity (which is very good for complexes **1** and **7**) is poor; ^1H NMR spectra of the reaction mixtures show extra signals that appear to be due to low molecular weight methyl methacrylate polymer. With **4** and **5** catalysis is clearly inefficient and

* The chirality of the N atoms could make this and related complexes potential candidates for the enantioselective addition of polyhalogenoalkanes to prochiral alkenes.

Table 1

The catalytic conversion of methyl methacrylate to its 1/1 CCl₄ adduct by various nickel triad complexes containing terdentate aryl ligands^a

| Entry | Complex | Metal/alkene (mol. %) | Temperature (°C) | Time (h) | Conversion (%) | Total turnover number (1/1 adduct/metal centre) |
|-------|-----------|-----------------------|------------------|----------|-------------------|---|
| 1 | 1a | 0.142 | 20 | 0.5 | 7 | 49 |
| 2 | 1a | 0.142 | 20 | 3.0 | 39 | 273 |
| 3 | 1a | 0.142 | 20 | 45.0 | 93 | 650 |
| 4 | 1b | 0.142 | 20 | 0.5 | 16 | 112 |
| 5 | 1b | 0.142 | 20 | 3.0 | 65 | 455 |
| 6 | 1b | 0.142 | 20 | 45.0 | 94 | 665 |
| 7 | 1c | 0.142 | 20 | 0.5 | 17 | 119 |
| 8 | 1c | 0.142 | 20 | 3.0 | 65 | 455 |
| 9 | 1c | 0.142 | 20 | 45.0 | 96 | 674 |
| 10 | 7 | 0.142 | 20 | 0.5 | 10 | 70 |
| 11 | 7 | 0.142 | 20 | 3.0 | 27 | 189 |
| 12 | 7 | 0.142 | 20 | 45.0 | 80 | 562 |
| 13 | 4 | 0.64 ^b | 65 | 12.0 | ~ 30 ^c | ~ 50 |
| 14 | 5 | 0.64 ^b | 65 | 12.0 | ~ 30 ^c | ~ 50 |
| 15 | 8 | 0.64 ^b | 65 | 0.5 | ~ 5 ^d | ~ 8 |
| 16 | 9 | 0.64 ^b | 65 | 0.5 | 0 ^{d,e} | 0 |
| 17 | 6 | 0.64 ^b | 65 | 3.0 | 0 ^f | 0 |
| 18 | 2 | 0.64 ^b | 65 | 3.0 | 0 | 0 |
| 19 | 3 | 0.64 ^b | 65 | 3.0 | <1 | <2 |

^a Determined by ¹H NMR. Reaction medium is 0.5 ml CH₃CN, 10 ml CCl₄ (excess), 2.5 ml methyl methacrylate (23.4 mmol) with 1/30 mmol metal complex unless otherwise stated; maximum turnover number possible is 702. ^b Reaction medium is 0.5 ml CH₃CN, 5 ml CCl₄ (excess), 0.5 ml methyl methacrylate (4.68 mmol) with 1/30 mmol metal complex; maximum turnover number possible is 156. ^c ~ 10% conversion to other materials. ^d Decomposition of metal complex occurs. ^e ~ 5% conversion to other materials. ^f ~ 25% conversion to other materials (see text).

free radicals seem to be leaving the metal coordination sphere and promoting alkene polymerization. The reason for this different reactivity of **4** and **5** compared to that of **1** must lie with the N-donor substituents and this difference can be most logically associated with steric bulk; the substituent size increases in the order Me < Et < i-Pr.

Based on these results it seems likely that for complexes **1**, **4** and **5** catalysis of the Kharasch reaction is an intimate process occurring at the metal centre with the steric effects of the ligand strongly influencing approach of substrates and reagents to the reactive site.

There is a report that even [NiX₂(PPh₃)₂] shows some catalytic activity for the Kharasch addition [7]. It was therefore thought worthwhile to test [Ni{C₆H₃(CH₂N(Me)Ph)₂-2,6}Br(PEt₃)₂] (**8**) and [Ni{C₆H₃(CH₂N(Me)-t-Bu)₂-2,6}Br(PEt₃)₂] (**9**) in which the nickel coordination sphere is completed by two monodentate P-donors rather than by the bis *ortho*-chelation of two N-donor atoms as found in **1**-**7**. Under the conditions employed (entries 15 and 16) only **8** generates some adduct (whereas **9** initiates some polymerization) and after 1 h at 65°C both species are fully decomposed and nickel salts precipitate. The phosphine complex [Ni{C₆H₃(CH₂-PPh₂)₂-2,6}Br] [**8**], which unlike **1** is not readily oxidised by CCl₄, also fails to catalyse the Kharasch reaction.

Interestingly, [Pd{C₆H₃(CH₂N(Me)Ph)₂-2,6}Br] (**6**), in which bis *ortho*-chelation

has been established by ^1H NMR, appears to promote alkene polymerization (entry 17), not addition of tetrachloromethane, and this aspect is being studied further. For completeness two palladium and platinum analogues of **1**, i.e. **2** ($\text{X} = \text{Br}$) and **3** ($\text{X} = \text{I}$), respectively, have also been screened. The stability of these two complexes to chlorinated solvents had suggested that they were not promising candidates for such catalysis and the negative results achieved (entries 18 and 19) confirm this expectation.

The nickel complexes **1a–1c** with terdentate $\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}$ are among the most effective complexes so far identified for effecting the catalytic Kharasch addition, and variation of the halide (and even introduction of a *para*-methoxy substituent) exert comparatively small effects on their capability. However, the introduction of bulkier N-donor substituents (e.g. Et, *i*-Pr) results in complexes with greatly reduced catalytic activity. These findings combined with earlier results [6] are consistent with the constraints imposed by a metal based mechanism in which free radicals do not enter the bulk solution, but react via innersphere pathways.

An outline for the operative mechanism of the catalytic sequence, shown schematically in Fig. 1, is as follows: firstly, the Ni^{II} -halide bond is broken, initiated by the large excess of potentially coordinating ligand L (CH_3CN or alkene), to generate an ion pair of the type $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}(\text{L})]^+ \text{X}^-$. Secondly, this ion pair activates the polyhalogenoalkane to form an innersphere complex. Two extreme possibilities for reaction progress are then (i) pure oxidative addition generating an octahedral Ni^{IV} cation of the type $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}(\text{CCl}_3)(\text{Cl})(\text{L})]^+$ or (ii) single electron transfer (SET) and ligand transfer oxidation to generate $[\text{Ni}^{\text{III}}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}(\text{Cl})(\text{L})(\text{CCl}_3)]^+$. Of these the second seems more likely because in a concerted reaction (neither CCl_4 nor methyl methacrylate alone appear to react with complexes **1**) the halocarbon radical could be trapped by a metal-bound

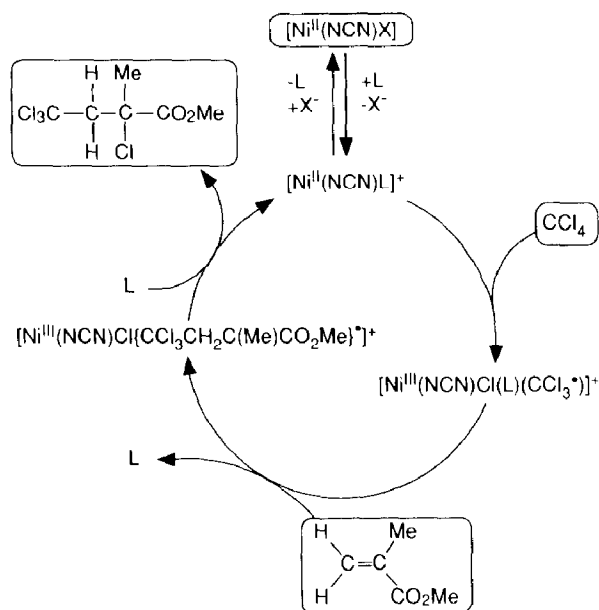


Fig. 1. The postulated catalytic cycle for the 1/1 addition of CCl_4 to methyl methacrylate using complexes **1**. L = CH_3CN or alkene, X = halide, and NCN = $\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}$.

alkene (L) to generate a nickel-bound $\{\text{CCl}_3\text{CH}_2\text{C}(\text{Me})\text{CO}_2\text{Me}\}^+$ unit. In a final stage transfer of Cl from the metal to this unit, i.e. Ni^{III} to Ni^{II} reduction, and elimination of the 1/1 adduct from the coordination sphere takes place. This type of mechanism has been studied and discussed in detail by Davis et al. [9].

Research in progress is directed to further elucidation of the role played by the R and R' N-donor substituents and to the application of arynickel complexes to chiral catalytic synthesis.

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