

Letter

New Homogeneous Catalysts in the Addition of Polyhalogenoalkanes to Olefins; Organonickel(II) Complexes [Ni{C₆H₃(CH₂NMe₂)₂-o,o'}X] (X = Cl, Br, I)

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The Karasch addition reaction of polyhalogenoalkanes to an alkene double bond, eqn. 1, is an important reaction of wide applicability that



X = halogen; Y = H, halogen, CF₃ or other electronegative group

generates a new carbon-carbon bond and introduces synthetically useful halide substituents. This addition can be promoted by free radical-forming precursors, and is also amenable to catalysis by various metal complexes including CuX [1], mono- and dinuclear carbonyl species (*e.g.* [Cr(CO)₃-(η⁶-C₁₀H₈) [2], [Fe(CO)₅] [3, 4] and [Fe(C₅H₅)(CO)₂]₂ [5]), [RuCl₂-(PPh₃)₃] [6, 7] and [MX₂(PPh₃)₂] (M = Ni, Pd) [6] as well as by the [Pd(OAc)₂]/PPh₃ system [8]. In contrast to the free radical-initiated reaction, which is liable to give telomers and polymers especially with activated alkenes, metal complex catalysis has the advantage of usually producing specifically a 1:1 alkene:halocarbon adduct. There are many applications of this reaction that are of industrial importance in the preparation of fine chemicals [1], and active research continues into the elucidation of the mechanisms operating in the various homogeneous metal-complex catalysed systems [9 - 13].

We now report that the square planar organonickel(II) amine species [Ni{C₆H₃(CH₂NMe₂)₂-o,o'}X] (**1a-c**; X = Cl, Br, I) [14], Fig. 1, are very active homogeneous catalysts for the Karasch addition under remarkably mild conditions. Some quantitative results relating to the **1a**-catalysed addition of the perhaloalkanes CCl₄, CBr₄, and CF₃CCl₃ to the terminal alkenes

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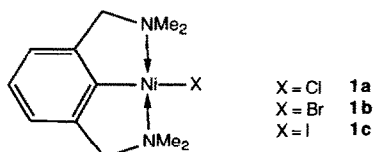


Fig. 1. The organonickel complexes $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}\}\text{X}]$ (**1a-c**)

TABLE 1

Reactions of polyhalogenoalkanes with alkenes catalysed by $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}\}\text{Cl}]$, **1a**, in $\text{CH}_3\text{CN}^{\text{a}}$

[Cat.] ^b (mol%)	CX ₃ Y	Alkene ^c	Time (h)	Temp. (°C)	Alkene conv. (%)	Specificity ^d (%)	Total turnover ^e
0.052 ^f	CCl ₄	MMA	72	25	90	100	1731
0.078 ^g	CCl ₄	MMA	18	30	70	100	897
0.78	CBr ₄	MMA	4	50	100	100	128
0.78	CF ₃ CCl ₃	MMA	4	60	95	100	122
0.78	CCl ₄	n-hept-1-ene	4	50	50	>95	64
0.78	CBr ₄	n-hept-1-ene	2	60	50	>95	64
0.78	CF ₃ CCl ₃	n-hept-1-ene	2	60	40	>95	51

^aReaction conditions: 0.5 ml CH_3CN , 25 mmol CX_3Y , 4.5 mmol alkene, 10 mg (3.5×10^{-2} mmol) **1a** unless otherwise stated.

^bWith respect to alkene.

^cMMA = methyl methacrylate.

^d1:1 adduct determined by ^1H NMR.

^e1:1 adduct/catalyst.

^f10 ml CH_3CN , 750 mmol CCl_4 , 135 mmol alkene, 20 mg (7×10^{-2} mmol) **1a**.

^g5 ml CH_3CN , 250 mmol CCl_4 , 45 mmol alkene, 10 mg (3.5×10^{-2} mmol) **1a**.

methyl methacrylate $[\text{CH}_2:\text{C}(\text{Me})\text{CO}_2\text{Me}]$, eqns. 2a-c, and hept-1-ene, eqns. 3a-c, are summarised in Table 1.

The addition of tetrachloromethane to methyl methacrylate in acetonitrile catalysed by less than 0.1 mol% of **1a** (relative to alkene) affords the 1:1 adduct $\text{CCl}_3\text{CH}_2\text{CCl}(\text{Me})\text{CO}_2\text{Me}$ (eqn. 2a) in high yield with 100% regio-specificity. A plot of percentage alkene conversion against time for a typical experiment employing 50 vol.% CH_3CN and 0.075 mol% of **1a** at 30 °C (Fig. 2) provides a turnover number of more than 500 h^{-1} for the first hour of reaction, with a total turnover number of 950 being achieved within 4 h. With 0.052 mol% of **1a**, total turnover numbers in excess of 1700 have been obtained after 72 h at 25 °C. The excellent activity of this organometallic species is further demonstrated by the fact that even at 0 °C (using an alkene:**1a** molar ratio of 120:1) catalytic conversion to the 1:1 adduct, though slow, was still found. The good catalytic reactivity and specificity of **1a** also applies to the 1:1 addition of CBr_4 and CF_3CCl_3 to methyl methacrylate, eqns. 2b and 2c. Furthermore, complexes **1** are effective catalysts for the 1:1 addition of CCl_4 , CBr_4 and CF_3CCl_3 to the non-activated terminal double bond of hept-1-ene, eqns. 3a-c. In these latter reactions, total

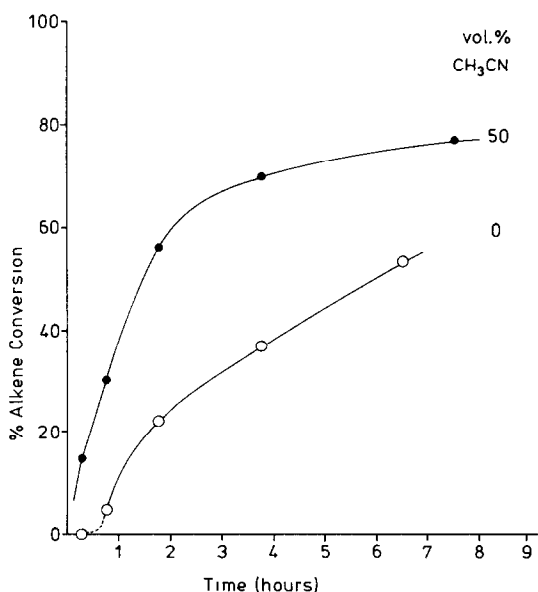
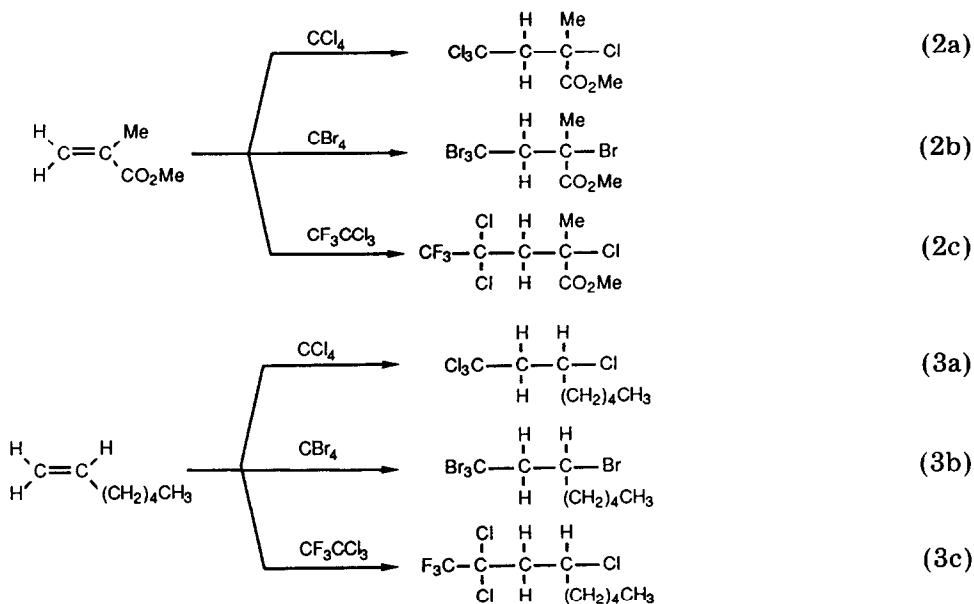


Fig. 2. The percentage conversion of methyl methacrylate to 1:1 adduct with CCl_4 at 30°C as a function of time for two different $\text{CH}_3\text{CN}/\text{CCl}_4$ ratios. Reaction conditions: 5 ml (46.8 mmol) methyl methacrylate, 10 mg (3.5×10^{-2} mmol) 1a, 25 ml CH_3CN + CCl_4 . 100% conversion corresponds to a total turnover number of 1337 per molecule 1a.

turnover numbers of 50 or more are readily obtained within a few hours under mild conditions and 1:1 adduct formation occurs with good regio-specificity (see Table 1).

The above results show that **1a** has a catalytic reactivity that is superior to that of $[\text{RuCl}_2(\text{PPh}_3)_3]$ [7], which is reported to be inactive below 40°C [8], and more than comparable to that of $[\text{Pd}(\text{OAc})_2]/\text{PPh}_3$ — the catalyst system reported to be the most active for the addition of CCl_4 to alkenes [8].

To determine the principle factors influencing the catalytic reactivity of our new system, various experiments have been carried out. For the CCl_4 /methyl methacrylate/ $\text{CH}_3\text{CN}/\mathbf{1a}$ case, the effect of the $\text{CH}_3\text{CN}/\text{CCl}_4$ ratio on the percentage alkene conversion has been studied at 30°C . Figure 3, which presents results after 105 min and 22 h reaction time, shows that optimal conversion rates are obtained with *ca.* 55 - 70 vol.% CH_3CN . A plot with a similar form was reported by Gandolfi and Cais on studying the effect of THF on the addition of CCl_4 to norbornadiene with naphthalene-chromiumtricarbonyl as catalyst [2].

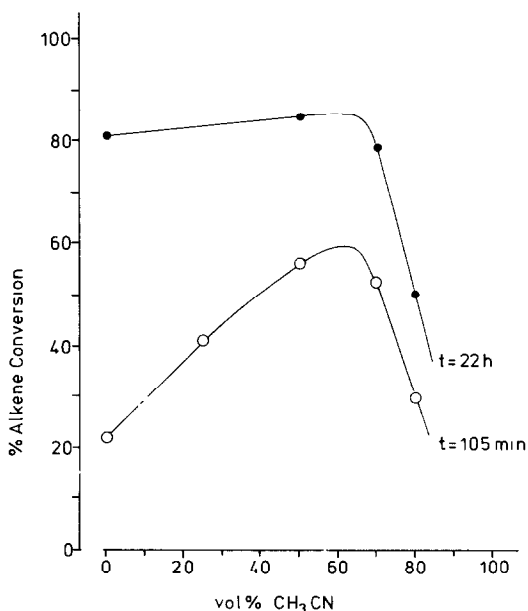


Fig. 3. The percentage conversion of methyl methacrylate to 1:1 adduct with CCl_4 at 30°C as a function of vol.% CH_3CN monitored at two different times. Reaction conditions as for Fig. 2.

In our system, although the initial rate of 1:1 adduct formation is dependent on the percentage of CH_3CN present, see Fig. 2, the final conversion of alkene to adduct ($t > 22\text{ h}$) is *independent* of this in the range 0 - 70 vol.% CH_3CN . Above 70 vol.% CH_3CN , where the CCl_4 :alkene ratio falls below 2:1 the final yield of adduct begins to drop rapidly. Note that CH_3CN is not essential for catalysis; in its absence, although the initial rate of adduct formation is somewhat lower (Fig. 2), the final percentage conversion is

appreciable. Under these latter conditions there is a noticeable induction period of several minutes, and it is possible that the role of the CH_3CN donor solvent in the initiation process is taken over by traces of moisture.

Apart from CH_3CN , other polar (donor) compounds such as diethyl ether, THF and pyridine are also satisfactory solvents for the catalysed 1:1 addition of CCl_4 to methyl methacrylate. It is not surprising, therefore, that the presence in the system of added water (in which species **1** are soluble without decomposition [14]) does not prevent catalysis.

The order of activity of the new Ni(II) catalysts in the addition of CCl_4 to methyl methacrylate is $1\text{a} > 1\text{b} > 1\text{c}$. The important role being played by the halide (X) of the catalyst is emphasised by the fact that the ionic species $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}\}(\text{CH}_3\text{CN})]\text{BF}_4$ does not exhibit catalytic activity. When catalysis using **1a** appears to be finished, solvated organonickel(III) species [15] (identified by UV/visible and ESR spectroscopic measurements) are present in the reaction medium. However, separate experiments have shown that the neutral Ni(III) complexes $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}\}\text{Br}_2]$ [15, 16] does not exhibit catalytic activity for the addition reaction of eqn. 1 under the conditions used for **1a** in Table 1.

Several aspects of the catalysis using complexes **1** point to the absence of free radicals in the bulk solution; there is no telomer formation, added galvinoxyl does not inhibit catalysis, and no cross-products are formed if a mixture of CCl_4 and CBr_4 is used. The operative mechanism is therefore likely to be one primarily based on intimate metal-centered reactions, as proposed for systems containing Cu(I) species [1, 13, 17] and $[\text{RuCl}_2(\text{PPh}_3)_3]$ [11], that can cycle the metal center between Ni(II) and Ni(III) oxidation states. Although details of this type of catalytic cycle require clarification, the involvement of carbon-centered radicals is almost certain. It is remarkable, therefore, that the organonickel species **1** can promote this type of addition reaction and at the same time still retain the potentially reactive $\text{Ni}^{\text{II}}\text{-C } \sigma\text{-bond}$.

Since the phosphine complexes $[\text{NiX}_2(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}$) have only limited activity in promoting the Karasch addition [7], we propose that the most important factor determining the electronic, chemical and catalytic properties of the Ni(II) centers in **1a-c** is the *trans* N-donor arrangement of the terdentate mono-anionic $\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}$ ligand. In particular this leads to the remarkably low Ni(II)/Ni(III) redox couple of +0.14 V (*vs.* SCE) for aqueous **1** (*cf.* Cu(I)/Cu(II), -0.08 V). It is worth mentioning here that a nickel(II) species with a different terdentate ligand providing a *trans* N-donor arrangement is reported to be an effective homogeneous catalyst in the water-gas shift reaction [18].

Our discovery that species **1** (with N-donor rather than carbonyl or phosphine ligands) are efficient homogeneous catalysts is a significant development which should lead to more interest being paid to the properties and applications of similar organometallic amine complexes. Moreover, in **1a-c** the specific, fairly rigid, N,C,N-tridentate chelation of the ligand to the metal and the consequent geometric restriction(s) imposed on the active

catalytic site(s) make these complexes well suited for future mechanistic investigations. Work in this and other areas of catalysis using derivatives and analogues of **1** is in progress.

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