Reactions of Bipyridyl-nickelacycloalkanes with Organic Halides

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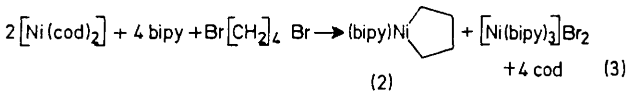
Summary Reactions of nickelacycloalkanes with organic halides and the synthesis of cycloalkanes, $\overline{[CH_2]_n\text{–}CHR}$, from $\alpha\omega$-dihalogenoalkanes, $X[CH_2]_nX$, and *gem*-dihalides, $RCHX_2$, with a nickel(0)–bipy complex are reported.

Organonickel compounds are widely used as reagents and catalysts in organic synthesis.[1] We recently reported[2] that a low valent nickel–bipyridyl complex is a powerful reagent for the cyclo-coupling of $\alpha\omega$-dihalogenoalkanes (equation 1), and suggested that the cyclo-coupling reaction might proceed through nickelacycloalkane intermediates. A recent paper[3] described the synthesis of a nickelacyclopentane complex by our method. We have also isolated the complex and now report the reactivities of these nickelacycloalkanes towards organic halides and a new preparative method for cycloalkanes from $\alpha\omega$-dihalides and *gem*-dihalides (equation 2).

$$X[CH_2]_nX \xrightarrow{\text{Ni}^0\text{–bipy}} \overline{[CH_2]_n} \qquad (1)$$

$$X[CH_2]_nX \xrightarrow[\text{(ii) }RCHX_2]{\text{(i) Ni}^0\text{–bipy}} \overline{[CH_2]_n\text{–}CHR} \qquad (2)$$

Addition of 1,4-dibromobutane (**1**) to the 2,2′-bipyridyl–bis(cyclo-octa-1,5-diene)nickel, [Ni(cod)$_2$], system (bipy : Ni molar ratio 2:1), in tetrahydrofuran (THF) at 0 °C produced a green solution containing bipyridyl-nickelacyclopentane (**2**) with precipitation of $Ni(bipy)_3Br_2$ (equation 3). Addition of n-hexane to the concentrated THF solution gave a dark green crystalline solid (**2**) which is soluble in THF and

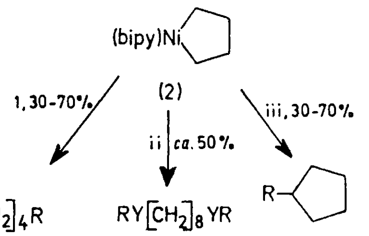


dimethoxyethane and sparingly soluble in benzene and ether. On treatment with oxygen and highly activated olefins, such as *p*-benzoquinone, dimethyl fumarate, or maleic anhydride, (**2**) liberated cyclobutane in 45—60% yields although it was uneffected by acrylonitrile[4] and carbon monoxide.[5] Deuterium chloride, acetic acid, and alcohols cleaved the Ni–C bond to give n-butane in quantitative yields. Reactions of (**2**) with several organic halides are shown in the Scheme. Alkyl halides (RX) gave the normal coupling products, R[CH$_2$]$_4$R, along with small amounts of cyclobutane, while acid halides and sulphonyl halides (RYX) gave octamethylene derivatives, RY[CH$_2$]$_8$YR, without formation of tetramethylene derivatives, RY[CH$_2$]$_4$YR. Treatment of (**2**) with *gem*-dihalides, such as methylene dibromide and ethylidene dibromide, resulted in the displacement of nickel to give cyclopentane derivatives. In a typical experiment, 2 mol of CH$_2$Br$_2$ were added at 0 °C under N$_2$ to a solution of (**2**), prepared *in situ* from 2 mol of [Ni(cod)$_2$], 6 mol of 2,2′-bipyridyl, and 1 mol of (**1**) in THF, and allowed to react at room temp. for 4 h, affording cyclopentane in 70% yield [based on (**1**)] with precipitation of [Ni(bipy)$_3$]Br$_2$. The best yield of cyclopentane was obtained with a molar ratio of (**1**) to the nickel complex of $< 0{\cdot}5:1$. An increase in the molar ratio of (**1**) : Ni reduced the yield of cyclopentane.

TABLE[a]

X[CH$_2$]$_n$X	RCHX$_2$	Product (yield, %)[b]
Br[CH$_2$]$_4$Br	CH$_2$Br$_2$	Cyclopentane (70)
Br[CH$_2$]$_4$Br	CH$_2$Cl$_2$	Cyclopentane (51)
Br[CH$_2$]$_4$Br	CH$_2$I$_2$	Cyclopentane (74)
Br[CH$_2$]$_4$Br	MeCHBr$_2$	Methylcyclopentane (59)
Br[CH$_2$]$_4$Br	CHCl$_3$	Chlorocyclopentane (27)
Br[CH$_2$]$_5$Br	CH$_2$Br$_2$	Cyclohexane (37)[c]
Br[CH$_2$]$_6$Br	CH$_2$Br$_2$	Cycloheptane (17)[d]

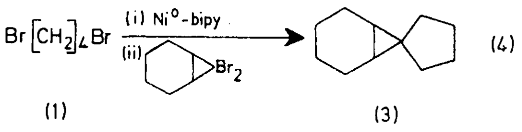
[a] Ni(cod)$_2$, 2 mmol; solvent THF, 10 ml; bipy : Ni molar ratio 3 : 1; X[CH$_2$]$_n$X : Ni molar ratio *ca.* 0·48—0·50 : 1; RCHX$_2$: Ni molar ratio 0·9—1·5 : 1. [b] Based on X[CH$_2$]$_n$X. [c] Cyclopentane was also formed in 38% yield. [d] Cyclohexane was also formed in 20% yield.



SCHEME. Reagents: i, RX: R = Et, $\mathrm{Pr^n}$, $\mathrm{Bu^n}$; ii, PhYX: Y = CO, SO$_2$; iii, RCHX$_2$: R = H, Me, Cl.

Similarly 1,5-dibromopentane and 1,6-dibromohexane with methylene dihalides gave cyclohexane and cycloheptane, respectively. In these cases, however, the yields were relatively low owing to the low stabilities of the metallocyclo intermediates and the low tendency for the formation of seven-membered ring.

This new method may have a potential application in the synthesis of cyclopentane derivatives, *e.g.* a combination of (**1**) and dibromonorcarane with the nickel complex successfully gave bicyclo[4.1.0]heptane-2-spirocyclopentane[6] (**3**) in 69% yield.



Dialkyl(bipyridyl)nickel complexes,[7] [R$_2$Ni(bipy)], prepared *in situ* from the $\mathrm{Ni^0}$–bipy and RBr (R = Et, $\mathrm{Pr^n}$ and $\mathrm{Bu^n}$) in THF also reacted with CH$_2$Br$_2$ to give the products RCH$_2$R in *ca.* 40% yields.

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