Reversible Oxidative Addition and Reductive Elimination of Diaryl Sulphide involving C–S Bond Cleavage and Formation: Exchange of Two Aryl Groups in Aryl(arylthiolato)nickel Complexes having Tertiary Phosphine Ligands

Kohtaro Osakada, Meguru Maeda, Yoshiyuki Nakamura, Takakazu Yamamoto,* and Akio Yamamoto

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Exchange between Ar and Ar′ groups in *trans*-$Ni(Ar)(SAr')(PEt_3)_2$ and *cis*-Ni(Ar)(SAr′)(dmpe) [dmpe = 1,2-bis-(dimethylphosphino)ethane] takes place to give a mixture of $Ni(SAr)(Ar')L_2$ and $Ni(Ar)(SAr')L_2$ *via* reversible reductive elimination and oxidative addition of diaryl sulphides involving C–S bond cleavage and formation at the Ni centre.

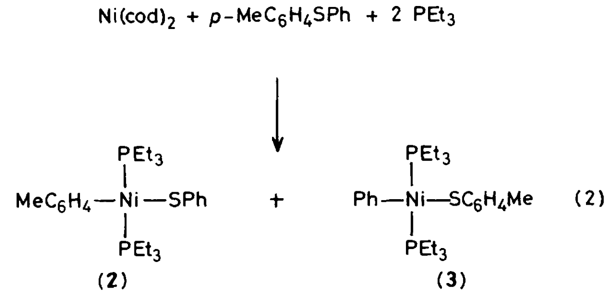
Cleavage and formation of a particular bond in organic compounds promoted by a transition metal complex are important elementary processes in catalytic reactions. Carbon–halogen bond cleavage has been most extensively studied and utilized,[1] and C–H bond cleavage is also attracting interest,[2] but processes involving cleavage of other bonds have received less attention. As an extension of our studies on carbon–oxygen bond cleavage and formation,[3] we now report the first example, to our knowledge, of rapid, reversible C–S bond cleavage and formation. The finding is relevant with respect to cross coupling of vinyl or aryl halides with thiolato anions to give organic sulphides.[4]

The C–S bond in diphenyl sulphide is readily cleaved on interaction with bis(cyclo-octa-1,5-diene)nickel(0) to give a phenyl(benzenethiolato)nickel(II) complex by oxidative addition, equation (1).

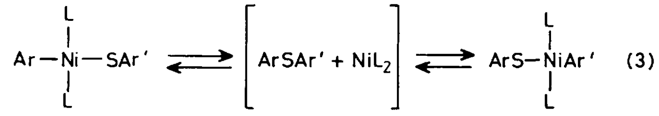
$$\mathrm{Ni(cod)_2 + PhSph + 2\,PEt_3 \longrightarrow \underset{(1)}{PhNi(SPh)(PEt_3)_2} + 2\,cod} \qquad (1)$$

cod = cyclo-octa-1,5-diene

In reactions of unsymmetrical diaryl sulphides with the Ni(0) complex, cleavage of a particular bond is observed. For example, the reaction of $\mathrm{MeC_6H_4SPh}$ with $\mathrm{Ni(cod)_2}$–$\mathrm{PEt_3}$ at room temperature gives a mixture of the complexes (**2**) and (**3**) in a ratio of 14 : 86. Complexes (**2**) and (**3**), as well as (**1**), were prepared independently by the treatment of aryl(methyl)nickel complexes[5] with thiophenols and were characterized on the basis of i.r. and n.m.r. (^{1}H and ^{31}P{^{1}H}) spectra as well as by elemental analysis.



(**2**) (**3**)



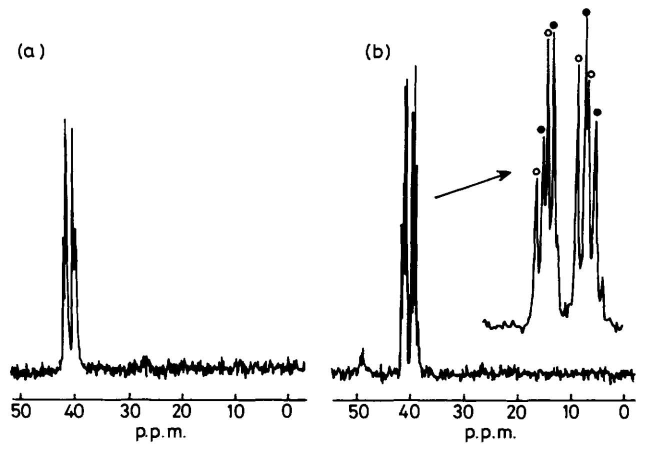
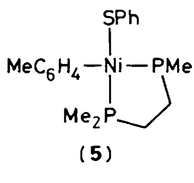
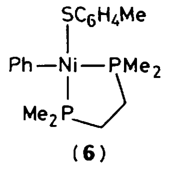


Figure 1. ^{31}P{^{1}H} n.m.r spectra of *cis*-Ni(Ar)(SAr′)(dmpe) (Ar, Ar′ = Ph-, *p*-$\mathrm{MeC_6H_4}$-) at 40 MHz in [^{2}H$_8$]toluene. (a) (**4**) at −40 °C. (b) A mixture of (**5**) and (**6**) at −40 °C; peaks marked ○ and ● each form AB patterns. On warming to room temperature a broad singlet is observed in both (a) and (b). Positive shifts are downfield from external $\mathrm{PPh_3}$.



(**5**)



(**6**)

Gradual transformation of (**2**) to (**3**) has been observed in the ^{1}H n.m.r. spectrum of a benzene solution of (**2**) at 60 °C. The reaction system reaches equilibrium in 25 h to give a mixture of (**2**) and (**3**) in a 1 : 1 ratio, which is different from the ratio of kinetic products obtained by oxidative addition. Heating (**3**) in benzene also gives a mixture of (**2**) and (**3**) in the same ratio. On raising the temperature, the equilibrium shifts slightly to favour the formation of (**3**). When (**1**) is heated in the presence of an equimolar amount of *p*-$\mathrm{MeC_6H_4SPh}$ at 78 °C for 6 h, a mixture of (**1**), (**2**), and (**3**) is obtained in a ratio of 2 : 1 : 1. The result suggests that reversible reductive elimination and oxidative addition of ArSAr′ occurs and isomerization between (**2**) and (**3**) proceeds through the mechanism in equation (3). The rate determining step in the isomerization is considered to be the reductive elimination. Configurational isomerization from the *trans* complex to its *cis* isomer may occur prior to the reductive elimination, although the ^{31}P{^{1}H} n.m.r. spectrum did not show formation of a detectable amount of the *cis*-isomer.

Addition of 1,2-bis(dimethylphosphino)ethane (dmpe) to a hexane solution of (**1**) gives *cis*-Ni(Ph)(SPh)(dmpe) (**4**) as yellow crystals. The ^{31}P{^{1}H} n.m.r. spectrum at −40 °C shows an AB quartet consistent with the presence of two inequivalent phosphorus nuclei (Figure 1). On warming to room temperature, the AB quartet turns into a broad singlet. A similar reaction of (**2**) with dmpe at room temperature (5 min reaction time) gives a mixture of two *cis* complexes, *cis*-Ni($\mathrm{C_6H_4Me}$)(SPh)(dmpe) (**5**) and *cis*-Ni(Ph)($\mathrm{SC_6H_4Me}$)-(dmpe) (**6**). The ^{31}P{^{1}H} n.m.r. spectrum indicates the mutual exchange of (**5**) and (**6**) on the n.m.r. time scale at room temperature. At −40 °C the exchange is so slow that peaks due to both (**5**) and (**6**) can be observed in the ^{31}P{^{1}H} n.m.r. spectrum.

The formation of (**6**) from (**2**) is explained by a reversible process which involves reductive elimination of ArSAr′ and at a later stage its oxidative addition to the *cis* complex under the mild conditions. Reductive elimination to give ArSAr′ should be more rapid in the *cis* complex than in the *trans* complex, with this step being rate determining. The rapid exchange between (**5**) and (**6**) on the n.m.r. time scale may involve anionic ligand (SAr) exchange processes.

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