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Preliminary communication

THE COORDINATION OF NICKEL(II) SALTS TO A SIMPLE OLEFIN IN A QUADRIDENTATE CHELATE

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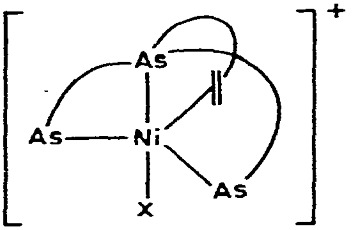
Summary

Simple NiX_2 (X = Cl, Br) salts form stable bonds with the olefin in bis(3-dimethylarsinopropyl)-3-butenylarsine; it is suggested that this stabilisation of Ni^{II}-olefin linkage is an electronic and not a chelate effect.

Coordination of olefins to such expensive metals as rhodium and palladium is important in a large number of industrial processes involving, for instance, oxidation, isomerisation, or hydrogenation of olefins [1]. We report here the results of some experiments involving attempts to coordinate the relatively inexpensive nickel(II) halides with multidentate ligands containing olefin groups, it appears that "hard" acids such as Ni^{II}, when suitable modified by such donors as trialkylarsines, may be persuaded to coordinate olefins.

There has been considerable interest in mixed olefin—Group VB chelates for some years [2] and recently tripod tetradentate chelates containing one phosphorus and three olefin groups have been shown to form trigonal bipyramidal complexes, [Rh(chelate)X], with rhodium(I) [3]. We have synthesised three ligands of the type $(CH_2{=}CHCH_2CH_2)_nAs(CH_2CH_2CH_2AsMe_2)_{3-n}$ (n = 1, tasol; n = 2, dasdol; n = 3, astol), and treated these with nickel(II) halides in ethanol. These ligands are similar, especially in possessing similar trigonal symmetry, to the tetratertiary arsine(qas) (n = 0) which forms trigonal bipyramidal complexes $[Ni(qas)X]^+$ in which all four donor sites are coordinated [4].

The triarsine—olefin ligand, tasol, readily reacts with NiX_2 to form deep blue-purple complexes of formula [Ni(tasol)X]Y (X = Cl, Br; Y = Cl, Br, ClO_4) and $[Ni(tasol)I_2]$. The former are 1/1 electrolytes in nitromethane and the latter is a non-electrolyte in this solvent. The free tasol ligand exhibits an IR band at 1640 cm^{-1}, assignable to "ν(C=C)", and in $[Ni(tasol)I_2]$ this absorption is clearly distinguishable at 1639 cm^{-1}, whereas it appears at 1590 cm^{-1} in the solid IR spectra of the $[Ni(tasol)X]^+$ (X = Cl, Br) complexes. Additional evidence for



$[Ni(tasol)X]^+$
(X = Cl, Br)

nickel—olefin coordination in the cationic species comes from their electronic spectra (in the solid state and in dichloromethane) which exhibit asymmetrical absorptions at 16.7 and 14.7×10^{-3} cm^{-1} (Cl) and 16.2×10^{-3} and 14.4×10^{-3} cm^{-1} (Br), very similar to the trigonal bipyramidal $[Ni(qas)X]^+$ species [4]. The spectrum of $[Ni(tasol)I_2]$ consists of an intense asymmetric band at 24.5×10^{-3} cm^{-1}, and as this is almost identical with that exhibited by $[Ni(tas)I_2]$ (tas = bis(3-dimethylarsinopropyl)methylarsine) [5], a square pyramidal molecule containing the As_3I_2 donor set, it is additional evidence that there is no nickel—olefin coordination in $[Ni(tasol)I_2]$. It is thus seen that nickel(II) salts act in a similar manner as do platinum(II) salts towards olefin systems, i.e. the tendency for the halide to displace the metal—olefin bond being $I \gg Br > Cl$ [6, 7].

With dasdol the only complexes isolable were of the type $[Ni(dasdol)_2X]^+$ (X = Cl, Br, I). All available evidence indicates that these complexes are pentacoordinate, contain the As_4X donor set, and there is no nickel—olefin coordination either in the solid state or in solution.

The triolefinarsine, astol, does not appear to react with nickel(II) salts [7].

In comparing the reactivity of these three potential quadridentate chelates towards nickel(II) salts it may be concluded: (i) that the expected "chelate effect' does not obtain, inasmuch as of these three ligands with trigonal symmetry only one acts as a tripod ligand promoting pentacoordinate trigonal bipyramidal $[Ni(ligand)X]^+$ complexes, and (ii) that the promotion of nickel—olefin coordination with tasol but not with dasdol would seem to indicate that, in the absence of the chelate effect of all three trigonally symmetrical ligands, it is the presence of the two arsenic atoms in the plane of the molecule which so modifies the relatively hard nickel(II) acid so that it can accept an olefin donor. The formation of a stable nickel(II)—olefin bond is even more remarkable in this system as it is known that the stability of olefin complexes decreases as the overall positive charge on the complex increases [8].

Acknowledgment

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Announcement

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