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Solution Behaviour of Ni(η^2-hex-1-ene){P(cyclohexyl)$_3$}$_2$ with Hex-1-ene, Studied by ^{31}P NMR Spectroscopy

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Bis- and mono-olefin nickel(0) complexes with tertiary phosphine, L, of the type Ni(ol)$_2$L and Ni(ol)L$_2$ respectively are known [1]. The equilibrium has been extensively studied by Tolman and

$$\mathrm{NiL_3 + ol \rightleftharpoons Ni(ol)L_2 + L} \qquad (1)$$

coworkers for L = PPh$_3$ [2]. However, no evidence has yet been given for the occurrence of the equilibrium

$$\mathrm{Ni(ol)L_2 + ol \rightleftharpoons Ni(ol)_2L + L} \qquad (2)$$

when, with respect to equilibrium (1), a second molecule of tertiary phosphine is displaced by an olefin. Here, we give evidence for the occurrence of equilibrium (2) when ol = hex-1-ene and L = P(cyclohexyl)$_3$.

Three NMR samples were prepared and sealed into 10 mm NMR tubes under strictly anaerobic conditions, at 10^{-6} mm Hg. The first tube contained 20 mg (0.028 mmol) Ni(η^2-hex-1-ene){P(cyclohexyl)$_3$}$_2$ [3] in 2 ml heptane/d_{12}-cyclohexane. Only a ^{31}P NMR signal due to Ni(η^2-hex-1-ene){P(cyclohexyl)$_3$}$_2$ was observed at room temperature at δ 35.0 and at −80 °C. The second tube contained 20 mg (0.028 mmol) Ni(η^2-hex-1-ene){P(cyclohexyl)$_3$}$_2$ and 30 μl (0.24 mmol) hex-1-ene in 2 ml heptane/d_{12}-cyclohexane. The ^{31}P NMR spectrum at room temperature showed two signals of equal intensity at δ 4.7 and δ 39.7 in addition to that due to Ni(η^2-hex-1-ene){P(cyclohexyl)$_3$}$_2$ at δ 35.0. On cooling to −100 °C, there was an increase in the intensities of the signals at δ 4.7 and δ 39.7. The third sample contained 17.8 mg (0.025 mmol) Ni(η^2-hex-1-ene){P(cyclohexyl)$_3$}$_2$ and 80 μl (0.64 mmol) hex-1-ene in 2 ml heptane/d_{12}-cyclohexane. It gave a ^{31}P NMR spectrum similar to that of the 30 μl hex-1-ene containing sample except that the signals at δ 4.7 and δ 39.7 were more intense. The signal at δ 4.7 is close in chemical shift to that previously reported for P(cyclohexyl)$_3$ [4]. This implies that the signal, of equal intensity, at δ 39.7, is due to a complex containing only one P(cyclohexyl)$_3$ ligand. The concentration of the species giving the signal at δ 39.7 is first order in hex-1-ene concentration giving a composition Ni(η^2-hex-1-ene)$_2$P(cyclohexyl)$_3$. The equilibrium constant for reaction (2) is 0.1 at room temperature and 0.18 at −100 °C showing that ΔH° for the equilibrium is very close to zero or that the equilibrium is very slowly obtained.

There are two unexpected observations about the ^{31}P NMR spectra of the complexes. The ^{31}P NMR spectra of Pd(η^2-hex-1-ene){P(cyclohexyl)$_3$}$_2$ and Pt(η^2-hex-1-ene){P(cyclohexyl)$_3$}$_2$ are AB at −100 °C (Pd) and 0 °C and below (Pt) [5]. For Pd(η^2-hex-1-ene){P(cyclohexyl)$_3$}$_2$, the ^{31}P NMR shifts are δ 34.2 and δ 31.9 with $^2J(^{31}\mathrm{P}, ^{31}\mathrm{P})$ = 38 Hz at −110 °C, while for Pt(η^2-hex-1-ene){P(cyclohexyl)$_3$}$_2$, they are δ 41.2, $^1J(^{195}\mathrm{Pt}, ^{31}\mathrm{P})$ = 3717 Hz, and δ 38.8, $^1J(^{195}\mathrm{Pt}, ^{31}\mathrm{P})$ = 3313 Hz, with $^2J(^{31}\mathrm{P}, ^{31}\mathrm{P})$ = 57 Hz at −20 °C. In contrast the ^{31}P NMR spectrum of Ni(η^2-hex-1-ene){P(cyclohexyl)$_3$}$_2$ is a singlet even at −100 °C. It is possible that the singlet is due to rapid olefin exchange, olefin rotation, or accidental degeneracy. The X-ray structure of Ni(η^2-C$_2$H$_4$)$_2$P(cyclohexyl)$_3$ shows a planar arrangement for the NiPC$_4$ skeleton [6]. In the case of Ni(η^2-hex-1-ene)$_2$P(cyclohexyl)$_3$, there are six isomers possible, ignoring the duplication of certain isomers due to optical activity. Only one major ^{31}P NMR signal is observed with a weak *ca.* 5%, signal at δ 41.8. It therefore appears that only one of the possible isomers is significantly populated although it is possible that the signal at δ 41.8 is an impurity and the isomers are rapidly interconverting, even at −100 °C or are accidently degenerate.

Unlike the nickel case, no M(η^2-hex-1-ene)$_2$P(cyclohexyl)$_3$ was detected by ^{31}P NMR for M = Pd and Pt by adding an excess of olefin to M(η^2-hex-1-ene){P(cyclohexyl)$_3$}$_2$. This is consistent with the known tendency of Ni(0) to form more stable olefin complexes than Pd(0) and Pt(0) [2].

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