The Stereochemistry of the Five-co-ordinate π-Allyl–Nickel Complex, π-$(CH_2CMeCH_2)Ni(diphos)Br$†

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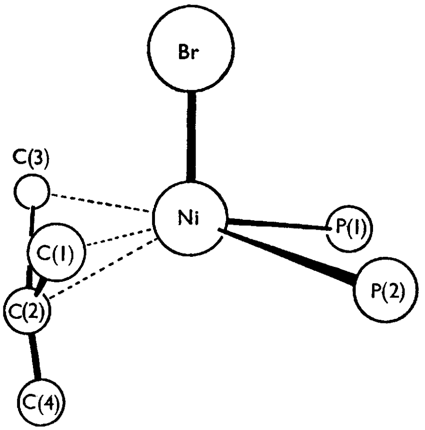
RECENT ^1H n.m.r. studies on square-planar π-allylpalladium complexes[1] (which have an outer configuration of sixteen electrons and may therefore be considered co-ordinatively unsaturated) indicate that an incoming donor ligand will tend to cause a π-allyl → σ-allyl conversion, rather than completing the eighteen outer-electron configuration for the metal. Similar tendencies are also observed in allyl–nickel systems where, again, it is found that retention of a square-planar co-ordination geometry is favoured.[2] Five-co-ordinate π-allylpalladium and π-allylnickel species are therefore rare, although a few examples have been reported.[3–4]

Methallyl[bis-1,2-(diphenylphosphino)ethane]-nickel bromide, prepared by the reaction of diphos† with 2-methyl-π-allylnickel bromide, is diamagnetic, air-stable, and shows a characteristic π-methallyl ^1H n.m.r. spectrum.[5] Due to the paucity of data on five-co-ordinate π-allylnickel complexes, and with a view to obtaining unequivocal information concerning the geometry of the nickel co-ordination sphere, we have undertaken a single-crystal *X*-ray structural analysis of this new complex.

π-$(CH_2CMeCH_2)Ni(diphos)Br$ crystallizes as deep red parallelepipeds in the triclinic space group $P\bar{1}$ (No. 2), the Delaunay-reduced[6] cell parameters being $a = 11{\cdot}13$, $b = 8{\cdot}17$, $c = 15{\cdot}41$ Å, $\alpha = 90{\cdot}8°$, $\beta = 96{\cdot}6°$, $\gamma = 105{\cdot}8°$. The observed density ($\rho_{obs} = 1{\cdot}46 \pm 0{\cdot}02$ g.cm.$^{-3}$) is consistent with the value calculated for $Z = 2$ ($\rho_{calc} = 1{\cdot}47$ g. cm.$^{-3}$). Complete three-dimensional data to $\sin\theta = 0{\cdot}38$ [Mo-K_α radiation] were collected on a 0·01°-incrementing Buerger Automated Diffractometer using the "stationary background, ω-scan, stationary background" technique. The structure was solved by conventional Patterson, Fourier, and least-squares refinement methods, the present discrepancy index being $R_F = 0{\cdot}104$ for 2782 independent reflections.

The co-ordination geometry of the nickel atom is shown in the Figure. If, as is customary, the π-allyl anion is regarded as occupying two co-ordination positions, the molecule may be described formally as a square-pyramidal Ni^{II} complex in which the π-allyl and diphos† ligands each occupy two (*cis*) basal sites and the bromine atom occupies the apical position. Important angles around the nickel(II) centre include: Br–Ni–P(1) = 96·4 ± 0·1°, Br–Ni–P(2) = 96·3 ± 0·1°, P(1)–Ni–P(2) = 88·8 ± 0·1°. If the line of intersection of the π-allyl ligand with the basal co-ordination plane of the nickel is assumed to be two-thirds the way along from the central [C(2)] to the terminal [C(1) and C(3)] atoms of the π-allyl ligand (as in the [π-$CH_2C(CO_2Et)CH_2NiBr]_2$ molecule[7]), then the nickel atom lies 0·34 Å above the basal plane, and the π-allyl ligand makes an angle of 106·5° with this plane (*cf.* 106·2° in the square-planar [π-$CH_2C(CO_2Et)CH_2NiBr]_2$[7]).



FIGURE

Nickel–carbon distances are Ni–C(1) = 2·059 Å, Ni–C(2) = 2·020 Å, Ni–C(3) = 2·049 Å (each ± 0·014 Å). Distances and angles within the π-methallyl ligand are: C(1)–C(2) = 1·423 ± 0·019 Å, C(2)–C(3) = 1·429 ± 0·019 Å, C(2)–C(4) = 1·547 ± 0·020 Å, ∠C(1)–C(2)–C(3) = 118·9 ± 1·3°, ∠C(1)–C(2)–C(4) = 119·5 ± 1·2°, ∠C(3)–C(2)–C(4) = 120·5 ± 1·2°. The 2-methyl group is displaced from the plane of the allyl group (and towards the nickel) by 0·26 Å, corresponding to an angular distortion of 9·5°. Similar anomalies have been reported in structural investigations of (π-$CH_2CMeCH_2)_2Ni$[8] and (π-$CH_2CMeCH_2)Pd(Ph_3P)Cl$[9] and presumably result from the non-orthogonality of the metal *d*-orbitals and the σ-framework of the allyl ligand.[10]

The nickel–bromine bond-length (2·671 ± 0·002 Å) is some 0·17 Å longer than the sum of the

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† diphos = bis-1,2-(diphenylphosphino)ethane.

Pauling covalent radii,[11] and is in good agreement with the Ni–Br(apical) bond-length found for the square-pyramidal complex

$Me_2As(CH_2)_3AsMe(CH_2)_3AsMe_2NiBr_2$,[12]

in which Ni–Br (apical) = 2·69 Å, and Ni–Br(basal) = 2·37 Å. Extension of the apical bond appears to be the rule with square-pyramidal complexes of spin-paired d^8 systems. Pd–Br distances in $(C_{14}H_{13}P)_3PdBr_2$[13] are 2·93 Å (apical), 2·52 Å (basal); Pd–As distances in $[Me_2AsC_6H_4AsMeC_6H_4AsMeC_6H_4AsMe_2PdBr^+]$ are 2·86 Å (apical), ~2·35 Å (basal); Pd–I distances in $[(Me_2PhP)_2PdI_2]_n$[15] are 3·28 Å (apical), 2·63 Å (basal).

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