Evidence for a Dissociative Mechanism in the Reaction of a Five-co-ordinate Nickel(II) Complex

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Summary Bis(diethyldithiophosphato)nickel(II) reacts with tributylphosphine to form a stable diamagnetic five-co-ordinate adduct; replacement of the tributylphosphine with bidentate ligands in benzene proceeds *via* a dissociative mechanism.

LITTLE quantitative information is available regarding the mechanism of ligand substitution at five co-ordinate centres.

Zink *et al.*[1] recently reported that the square planar complex bis(diethyldithiophosphato)nickel(II) [$Ni(dtp)_2$, dtp = $(EtO)_2PS_2^-$] forms a 1:1 adduct with triphenylphosphine. This adduct is, however, very unstable ($K_f = ca.$ $1\ \text{M}^{-1}$). We found that the addition of PBu_3 to a solution of $Ni(dtp)_2$ in benzene causes a deep purple colour to develop instantly, $\lambda_{max} = 554$ nm ($\epsilon = 400$). A Job's continuous variations study clearly shows that a 1:1 complex is formed. The adduct is quite stable, $K_f = 10^4\ \text{M}^{-1}$ at 25°C in benzene. Tributyl phosphite also forms a 1:1 adduct with $Ni(dtp)_2$, $K_f = ca.$ $40\ \text{M}^{-1}$. In contrast to the reported PPh_3 adduct the PBu_3 complex is low spin, having $\chi_m = ca.\ 500 \times 10^{-6}$ cgs at room temperature in solution. This small positive susceptibility compares favourably with values found for other low-spin five-co-ordinate complexes.[2] Preparation of the adduct in benzene followed by evaporation of the solvent results in a rather stable purple oil which is essentially diamagnetic and yields an electronic spectrum identical to that of a solution freshly prepared from $Ni(dtp)_2$ and PBu_3.

The electronic spectrum consists simply of a broad band centred at 554 nm. This supports[2,3] the expected square pyramidal structure with the visible band being due to:

$$^1E \longleftarrow {}^1A_1\ (d_{x^2-y^2} \longleftarrow d_{xz,yz}).$$

The kinetics of the replacement of the PBu_3 group by bipyridine (bipy), 1,10-phenanthroline (phen), 1,2-bis(diphenylphosphino)ethane (diphos), and *cis*-1,2-bis(diphenylphosphino)ethylene (VPP) was followed at 25°C in benzene with a Durrum stopped-flow apparatus. Pseudo-first order conditions were used. The initial rapid reaction is the replacement of PBu_3 yielding six-co-ordinate adducts.[4] This is followed by a much slower replacement of the dtp groups yielding a dtp$^-$ salt which precipitates from solution.

We found that plots of k_{obs} *vs.* concentration of nucleophile in general showed pronounced curvature (Table) with all k_{obs} values tending towards the same limit regardless of the nucleophile. The addition of excess PBu_3 to the solution lowered the k_{obs} values but did not affect the limit. Over the initial linear portions of the plots we found $k_{\text{obs}} \propto 1/[PBu_3]$ for a fixed nucleophile concentration. Frequently with no excess PBu_3 present the reactions showed deviation from good first-order kinetics. This simply indicates that the nucleophile and PBu_3 are competing for some intermediate. We propose the following mechanism:

$$Ni(dtp)_2PBu_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ni(dtp)_2 + PBu_3$$

$$Ni(dtp)_2 + L\text{–}L \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Ni(dtp)_2\text{–}L\text{–}L \xrightarrow{k_5} Ni(dtp)_2(L\text{–}L)$$

Using the steady state approximation for $Ni(dtp)_2$ and $Ni(dtp)_2$–L–L, the mechanism yields equation (1) which predicts a limiting rate constant of k_1. This limit is, of

$$k_{\text{obs}} = \frac{k_1k_3k_5[L\text{–}L]}{k_2[PBu_3](k_4 + k_5) + k_3k_5[L\text{–}L]} \qquad (1)$$

course, independent of nucleophile and is 225 ± 50 s^{-1}. The mechanism predicts that $k_{\text{obs}} \propto 1/[PBu_3]$ when k_{obs} is linear in [L–L] and this was observed. We found that the relative reactivities are diphos > VPP >> phen > bipy. Diphos is so reactive that the $[PBu_3]$ dependence is small unless a huge excess is present. With no excess PBu_3 k_{obs} is independent of [diphos] and is simply equal to k_1. Plots of $1/k_{\text{obs}}$ *vs.* 1/[L–L] were linear as required by equation (1) all yielding the same intercept $(1/k_1)$ regardless of the amount of excess PBu_3 present. The slopes of such plots simply indicate the probability that the intermediate will return to react or go on to product.

TABLE[a]

Nucleophile, L	k_{obs}/s^{-1}	Range of [L]/ M × 10^3
diphos[b]	$275[L]/([L] + 0{\cdot}76 \times 10^{-3})$	2—20
VPP[b]	$230[L]/([L] + 23 \times 10^{-3})$	2—20
bipy[c]	$200[L]/([L] + 1200 \times 10^{-3})$	10—300
phen[c]	$295[L]$	5—50

[a] Benzene, 25 °C. $[Ni(dtp)PBu_3]$ is 2×10^{-4} to 5×10^{-4} M. [b] Excess $PBu_3 = 2{\cdot}5 \times 10^{-3}$ M' [c] Excess $PBu_3 = 5{\cdot}3 \times 10^{-3}$ M.

It is easy to show that an associative pathway is not important in these reactions. Regardless of the details of the reaction sequence, an associative mechanism would not yield a limiting rate constant independent of either the nucleophile or PBu_3 concentration.[5] Since an associative pathway cannot contribute at high nucleophile concentrations, it is unimportant at any concentration.

Although this initial study clearly shows a dissociative mechanism for substitution at a five-co-ordinate centre, we do not believe this will be the general case. Indeed it has already been suggested that this is not the case.[5] In addition we have found[5] in this laboratory that the substitution reactions of the five-co-ordinate dithiolene complexes $M(S_2C_2Ph_2)_2PR_3$ and $M[S_2C_2(CN)_2]_2PR_3^-$ (M = Co, Fe) definitely do not follow the dissociative mechanism found for $Ni(dtp)_2PBu_3$.

In the case of nickel(II) we suspect that low-spin square pyramidal complexes will substitute *via* a dissociative pathway because a S_N2 mechanism requires an initial spin change in the reaction sequence. However, high-spin square pyramidal nickel(II) does not have this problem and we look for associative pathways to appear. The argument that 18 electron systems will react *via* S_N1 mechanisms in our view will apply only to low-spin systems because, for example, many stable high-spin 20 electron systems are known—octahedral nickel(II).

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