

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

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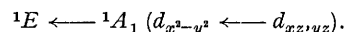
*Summary* Bis(diethyldithiophosphato)nickel(II) reacts with tributylphosphine to form a stable diamagnetic five-co-ordinate adduct; replacement of the tributylphosphine with bidentate ligands in benzene proceeds *via* a dissociative mechanism.

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

Zink *et al.*<sup>1</sup> recently reported that the square planar complex bis(diethyldithiophosphato)nickel(II) [Ni(dtp)<sub>2</sub>, dtp = (EtO)<sub>2</sub>PS<sub>2</sub><sup>-</sup>] 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<sub>3</sub> to a solution of Ni(dtp)<sub>2</sub> in benzene causes a deep purple colour to develop instantly,  $\lambda_{\text{max}} = 554 \text{ nm}$  ( $\epsilon = 400$ ). 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)<sub>2</sub>,  $K_f = ca. 40 \text{ M}^{-1}$ . In contrast to the reported PPh<sub>3</sub> adduct the PBu<sub>3</sub> complex is low spin, having  $\chi_m = ca. 500 \times 10^{-6}$  cgs at room temperature in solution.

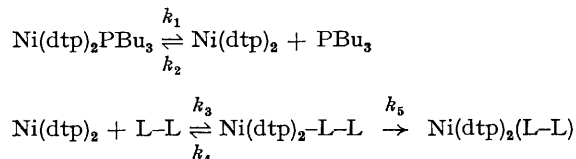
This small positive susceptibility compares favourably with values found for other low-spin five-co-ordinate complexes.<sup>2</sup> Preparation of the adduct in benzene followed by evaporation of the solvent results in a rather stable purple oil which is essentially diamagnetic and yields an electronic spectrum identical to that of a solution freshly prepared from Ni(dtp)<sub>2</sub> and PBu<sub>3</sub>.

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



The kinetics of the replacement of the PBu<sub>3</sub> 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<sub>3</sub> yielding six-co-ordinate adducts.<sup>4</sup> This is followed by a much slower replacement of the dtp groups yielding a dtp<sup>-</sup> salt which precipitates from solution.

We found that plots of  $k_{\text{obs}}$  vs. concentration of nucleophile in general showed pronounced curvature (Table) with all  $k_{\text{obs}}$  values tending towards the same limit regardless of the nucleophile. The addition of excess  $\text{PBu}_3$  to the solution lowered the  $k_{\text{obs}}$  values but did not affect the limit. Over the initial linear portions of the plots we found  $k_{\text{obs}} \propto 1/[\text{PBu}_3]$  for a fixed nucleophile concentration. Frequently with no excess  $\text{PBu}_3$  present the reactions showed deviation from good first-order kinetics. This simply indicates that the nucleophile and  $\text{PBu}_3$  are competing for some intermediate. We propose the following mechanism:



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

$$k_{\text{obs}} = \frac{k_1 k_3 k_5 [\text{L-L}]}{k_2 [\text{PBu}_3] (k_4 + k_5) + k_3 k_5 [\text{L-L}]} \quad (1)$$

course, independent of nucleophile and is  $225 \pm 50 \text{ s}^{-1}$ . The mechanism predicts that  $k_{\text{obs}} \propto 1/[\text{PBu}_3]$  when  $k_{\text{obs}}$  is linear in  $[\text{L-L}]$  and this was observed. We found that the relative reactivities are  $\text{diphos} > \text{VPP} \gg \text{phen} > \text{bipy}$ . *Diphos* is so reactive that the  $[\text{PBu}_3]$  dependence is small unless a huge excess is present. With no excess  $\text{PBu}_3$   $k_{\text{obs}}$  is independent of  $[\text{diphos}]$  and is simply equal to  $k_1$ . Plots of  $1/k_{\text{obs}}$  vs.  $1/[\text{L-L}]$  were linear as required by equation (1) all yielding the same intercept ( $1/k_1$ ) regardless of the amount of excess  $\text{PBu}_3$  present. The slopes of such plots simply indicate the probability that the intermediate will return to react or go on to product.

TABLE<sup>a</sup>

Nucleophile, L	$k_{\text{obs}}/\text{s}^{-1}$	Range of $[\text{L}]/$ $\text{M} \times 10^3$
diphos <sup>b</sup>	$275[\text{L}]/([\text{L}] + 0.76 \times 10^{-3})$	2—20
VPP <sup>b</sup>	$230[\text{L}]/([\text{L}] + 23 \times 10^{-3})$	2—20
bipy <sup>c</sup>	$200[\text{L}]/([\text{L}] + 1200 \times 10^{-3})$	10—300
phen <sup>c</sup>	$295[\text{L}]$	5—50

<sup>a</sup> Benzene, 25 °C.  $[\text{Ni}(\text{dtp})\text{PBu}_3]$  is  $2 \times 10^{-4}$  to  $5 \times 10^{-4} \text{ M}$ .  
<sup>b</sup> Excess  $\text{PBu}_3 = 2.5 \times 10^{-3} \text{ M}$  <sup>c</sup> Excess  $\text{PBu}_3 = 5.3 \times 10^{-3} \text{ M}$ .

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  $\text{PBu}_3$  concentration.<sup>5</sup> 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.<sup>5</sup> In addition we have found<sup>5</sup> in this laboratory that the substitution reactions of the five-co-ordinate dithiolene complexes  $\text{M}(\text{S}_2\text{C}_2\text{Ph}_2)_2\text{PR}_3$  and  $\text{M}[\text{S}_2\text{C}_2(\text{CN})_2]_2\text{PR}_3^-$  ( $\text{M} = \text{Co}, \text{Fe}$ ) definitely do not follow the dissociative mechanism found for  $\text{Ni}(\text{dtp})_2\text{PBu}_3$ .

In the case of nickel(II) we suspect that low-spin square pyramidal complexes will substitute *via* a dissociative pathway because a  $\text{S}_{\text{N}}2$  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*  $\text{S}_{\text{N}}1$  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).

(Received, 25th April 1973; Com. 585.)

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