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Reactions of Nickel Dialkyldithiophosphates with Phosphines

LESLEY F. BLACK

Chemistry Department, W. S. and L. B. Robinson University College, Broken Hill, N. S. W. 2880, Australia

DOUGLAS P. GRADDON*

School of Chemistry, University of New South Wales, Kensington, N. S. W. 2033, Australia

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The high-spin, 6-coordinate adducts of heterocyclic bases with nickel(II) complexes of O,O′-dialkyldithiophosphates have been long known [1] and studies of the adduct formation equilibria in solution show that two molecules of bases, such as pyridine, add successively with $K_1 < K_2$ and $\Delta H_1 \simeq \Delta H_{1+2}$ [2, 3]. Addition of phosphines has been less well studied but a dark green, high-spin, 5-coordinate 1:1 adduct of triphenylphosphine with $[(EtO)_2PS_2]_2Ni$ has been described [4] and the corresponding adduct with tributylphosphine has been obtained as a deep purple oil with a low-spin configuration [5]. Kinetic studies have been made of the replacement of PBu_3 in this adduct by bidentate bases: with 2,2′-bipyridine or 1,10-phenanthroline the products are the known high-spin, 6-coordinate, *cis*-octahedral heterocyclic base adducts, but with 1,2-bis(diphenylphosphino)-ethane (diphos) or *cis*-1,2-bis(diphenylphosphino)-ethene the reaction products are of unknown constitution [6].

As part of an extended study of the thermodynamics of adduct formation by low-spin nickel(II) complexes we were interested to obtain data for the addition of phosphines to the dithiophosphates and have carried out calorimetric titrations of several nickel(II) dithiophosphates with different phosphines.

Preliminary spectrophotometric and magnetic studies of reactions with PBu_3 in benzene solution confirmed the previous observation [5] that low-spin 1:1 adducts of high stability were formed and calorimetric titrations of 1–5 × $10^{-3}M$ solutions of the nickel complexes gave the following thermodynamic data for adduct formation in benzene at 30 °C:

	K	$-\Delta H^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$
$[(MeO)_2PS_2]_2Ni$	$>10^4$	54.8 ± 1.1	>23.2	<104
$[(EtO)_2PS_2]_2Ni$	$>10^4$	55.7 ± 0.6	>23.2	<107
$[(CxO)_2PS_2]_2Ni$	2060 ± 180	55.8 ± 0.1	19.2 ± 1.1	121 ± 1

where K is in l mol^{-1}, ΔH and ΔG in kJ mol^{-1} and ΔS in J K^{-1} mol^{-1}; Cx = cyclohexyl.

It is interesting to compare these data for the formation of low-spin 1:1 adducts with those previously obtained for corresponding high-spin adducts: for $[(EtO)_2PS_2]_2Ni{\cdot}PPh_3$ K ~ 1 [4]; for $[(EtO)_2PS_2]_2Ni{\cdot}py$ K = 15, $-\Delta H^\circ = 73$ [3] and for $[Ph_2PS_2]_2Ni{\cdot}py$ K = 500, $-\Delta H^\circ = 34$ [7]. The enthalpies of formation of the low-spin PBu_3 adducts are in the same range as those of the high-spin adducts, but the PBu_3 adducts are of much higher stability.

Spectrophotometric Job continuous variation studies showed that the phosphines Cx_3P, Me_2PPh and $MePPh_2$ also formed 1:1 adducts with the dimethyldithiophosphate in benzene solution, characterised by an absorption band of high intensity ($\epsilon \sim 1500$) at about 550 nm, like that of the PBu_3 adduct. The adducts with these phosphines were however much less stable, the following stability constants being obtained spectrophotometrically:

Phosphine	Me_2PPh	$MePPh_2$	Cx_3P
K (l mol^{-1})	2900 ± 250	157 ± 4	~10

The deep purple solutions of the adducts were also found to be unstable in the presence of excess base and attempts to determine enthalpies of adduct formation by calorimetry gave quite unexpected results. With Me_2PPh all three nickel complexes gave enthalpograms showing quantitative reaction with 7–8 equivalents of phosphine and the liberation of 700–800 kJ (g. at-Ni)$^{-1}$ of heat (Fig. 1). At the end of the titration the solutions were brown, but a deep purple colour could be restored by passing air through the solutions. With $MePPh_2$ or Cx_3P a small heat change at the beginning of the titration was followed by the evolution of much heat, again requiring reaction with many equivalents of phosphine (Fig. 1). It is clear that in these cases initial adduct formation is followed by some other reaction, probably reduction of the nickel compound by the phosphine.

Like PBu_3, diphos reacted quantitatively ($K > 10^5$) with all three nickel compounds according to 1:1 stoichiometry, with the following enthalpies of reaction:

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*Author to whom correspondence should be addressed.

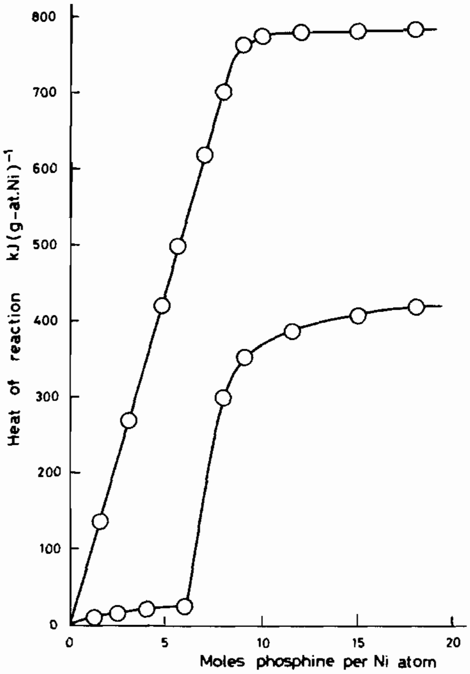


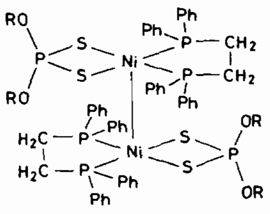
Figure 1. Calorimetric titration of $[(EtO)_2PS_2]_2Ni$, 1.4 × $10^{-3}M$ with Me_2PPh (upper curve) and 9 × $10^{-4}M$ with $MePPh_2$ (lower).

R in $[(RO)_2PS_2]_2Ni$	Me	Et	Cx
$-\Delta H°$ (kJ mol^{-1})	92 ± 4	77 ± 2	63 ± 2

The solutions produced were orange-yellow, the two absorption bands of the nickel compound at 520 and 680 nm being replaced by new high-intensity absorption in the near UV region. On standing these solutions deposited orange crystals, shown by analysis to be $(RO)_2PS_2Ni$·diphos:

R =		Me	Et	Pr	Cx
C%	found	54.5	55.0	59.0	61.8
	required	54.8	56.1	57.3	60.8
H%	found	4.8	4.9	5.5	6.4
	required	4.9	5.3	5.7	6.2
P%	found	14.8	14.5	13.7	12.8
	required	15.1	14.5	13.9	12.4
S%	found	10.3	9.6	9.8	9.3
	required	10.4	10.0	9.6	8.5
Ni%	found	9.6	9.1	9.1	8.4
	required	9.6	9.1	8.8	7.9

All four orange solids had m.p.'s close to 260 °C. Infra-red spectra were complex, but all observed bands could be found in the spectra of either $[(RO)_2PS_2]_2Ni$ or diphos. The compounds are formally derivatives of nickel(I), but were found to be diamagnetic, both in the solid state and in solution. Attempts to determine molecular weights were frustrated by low solubilities. In view of these findings the most likely structures for these compounds appear to be either Ni–Ni bonded dimers (I) or bridged dimers analogous to copper(II) acetate (II)



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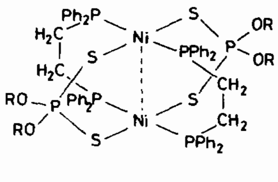

II

Experimental

Nickel(II) dialkyldithiophosphate complexes were prepared from the alcohols, phosphorus pentasulphide and nickel(II) chloride and purified by crystallisation. Purity was checked by C, H and Ni analysis. Calorimetric titrations were carried out in a LKB 8700 calorimeter by the previously described technique [8]. At least three titrations were done in each system and the values of ΔH° are averages with mean deviations; values of K are the average of at least three determinations at different nickel concentrations in the range 1–6 × $10^{-3}M$ and uncertainties in K are the sum of mean deviations from the average and the average of the standard deviations in individual titrations.

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