Bull.Chem.Soc.Ethiop.,5(2), 73-79 (1991).

REACTIONS OF FOUR COORDINATE NICKEL(II) PHOSPHINE COMPLEXES WITH ELEMENTAL SULPHUR

James Darkwa*[a], Wilfred A.A. Ddamba[a] and Lenore M. Koczon[b]
[a]Department of Chemistry, University of Botswana
Private Bag 0022, Gaborone, Botswana
[b]Department of Mathematics and Natural Sciences
Northern State University, Aberdeen, South Dakota, U.S.A.

(Received May 17, 1991; revised September 30, 1991)

ABSTRACT. At room temperature or under reflux, elemental sulphur reacts with $NiX_2(PPh_3)_2$ (X = Cl, Br, I, NO_3, SCN) or $NiCl(PPh_3)(dtc)$ (dtc = diethyldithiocarbamate, S_2CNEt_2) to give $SPPh_3$. The reactions with $NiX_2(PPh_3)_2$ also give NiX_2 as the other product. The reaction with $NiCl(PPh_3)(dtc)$ involves rearrangement, leading to the formation of $NiCl_2$ and $Ni(dtc)_2$. Formation of $SPPh_3$ in these reactions indicates that they might involve intermediates where $SPPh_3$ functions as a coordinated ligand. The $NiCl(PPh_3)(dtc)$ reaction is first order with a rate constant of 10.8×10^{-3} min^{-1} at 30.5°C.

INTRODUCTION

The reaction of elemental sulphur with low-valent transition metal complexes is an area of current research interest. This is because such reactions lead to the formation of metal sulphides which have potential use as catalysts [1,2] and in material science [3]. The importance of metal sulphides has also been identified in metalloproteins [4]. Special interest in nickel-sulphur chemistry in particular is a result of nickel having been identified at the active site of several hydrogenases [5] and the discovery that Raney nickel can desulphurize organic thiols [6,7].

Our interest in the reaction of sulphur with nickel phosphine complexes stems from the following: sulphur reacts with $Ni(CO)_4$ [8] and $[(C_5H_5)Ni(CO)]_2$ [9] to form cluster compounds, containing bridging sulphur ligands. In addition to these complexes, other cluster compounds with bridging sulphur ligands have been synthesized when H_2S or $(Me_3Si)_2S$ is reacted with nickel compounds in the presence of phosphines [10-12]. Recently Sato and coworkers have synthesized $[Ru(C_5H_4S)_2S]Ni(PPh_3)$, a complex containing bridging sulphur, from $Ru(C_5H_4S)_2S$ and $Ni(PPh_3)_4$ [13]. Other nickel group compounds, such as $Pt(SH)_2(PPh_3)_2$ [14] and $Pt(PPh_3)_4$ [15-16], form $Pt(S_4)(PPh_3)_2$ when reacted with sulphur. The above information points to the possibility of nickel phosphine complexes reacting with sulphur to produce nickel sulphide complexes. We have investigated the reactions of nickel phosphine complexes with sulphur, expecting to obtain nickel sulphide complexes. The results of our study, which did not proceed as anticipated, are reported here.

EXPERIMENTAL

Materials and instrumentation. All solvents used were reagent grade. Dichloromethane was dried and distilled over P_2O_5. Hexane and toluene were dried and distilled over sodium. $NiX_2(PPh_3)_2$ and $NiCl(PPh_3)(dtc)$ were prepared by the established literature procedures [17-18].

Infrared spectra were recorded on a Pye Unicam SP3-300S or a Mattson Polaris/Icon FT-IR. UV/vis and ^1H NMR spectra were recorded on Hitachi 15020 and IBM instruments NR/80 FT-NMR, respectively. ^1H NMR chemical shifts were referenced to the solvent ($CHCl_3$, 7.26 ppm) or TMS. Elemental analyses were performed by C.H.N. Analysis Limited, Leicester, England.

Reactions of $NiX_2(PPh_3)_2$ (X = Cl, Br, I, NO_3 and SCN) with elemental sulphur. In a typical experiment, a mixture of $NiBr_2(PPh_3)_2$ (1.00 g, 1.35 mmol) and sulphur (0.086 g, 0.335 mmol) in CH_2Cl_2 (50 ml) was refluxed for 1 hr. The cream coloured precipitate of $NiBr_2$ was isolated by suction filtration and washed with CH_2Cl_2 (10 ml). Yield 0.30 g. The filtrate was concentrated to about 10 ml and hexane (5 ml) was added. The resultant solution was cooled in a freezer to about -15°C overnight to give white crystalline $SPPh_3$, which was isolated and dried by suction filtration. Yield 0.73 g,(92%). Anal. calcd. for $C_{18}H_{15}PS$ C, 73.45; H, 5.14; P, 10.52; S,10.89. Found : C, 73.46; H,5.21; P,10.36; S, 10.97.

Reaction of $NiCl(PPh_3)(dtc)$ with elemental sulphur: formation of $NiCl_2$ and $Ni(dtc)_2$. To a solution of $NiCl(PPh_3)(dtc)$ (1.00 g, 2.03 mmol) in CH_2Cl_2 (40 ml) was added sulphur (0.065 g, 0.254 mmol). The mixture was refluxed for 4 hrs and filtered to isolate 0.135 g pale green $NiCl_2$. The filtrate was pumped dry and toluene (50 ml) was added to the residue. The sparingly soluble green $Ni(dtc)_2$ was isolated by suction filtration. Yield 0.29 g, (81%). The filtrate was then pumped dry and the residue recrystallized from (2:1) CH_2Cl_2 / hexane at -15°C to give $SPPh_3$. Yield 0.57 g, (95%).

Kinetic experiment. The kinetics of the reaction of $[NiCl(PPh_3)(dtc)]$ with sulphur were studied at 30.5°C at concentrations 1.50×10^{-6} M and 5.85×10^{-6} M respectively in CH_2Cl_2. The disappearance of $NiCl(PPh_3)(dtc)$ was monitored by UV/vis spectroscopy at 512 nm. The data were processed on a Macintosh SE FDHD personal computer, with the kinetic program *Kinitics* [19].

RESULTS AND DISCUSSION

Solutions of $NiX_2(PPh_3)_2$ in CH_2Cl_2 rapidly form $SPPh_3$ and NiX_2 when reacted with elemental sulphur at elevated temperatures, as shown in equation (1).

$$NiX_2(PPh_3)_2 + \tfrac{1}{4} S_4 \rightarrow NiX_2 + SPPh_3 \qquad (1)$$

The first visible sign of reaction is seen within 5 min of mixing. The reaction is slower at room temperature, but visible changes are obvious within 30 min. Formation of NiX_2 is nearly quantitative (Table 1). All solids of NiX_2 could dissolve in H_2O to form $[Ni(OH_2)_6]^{2+}$. The hexa-aquo complex was then identified by its characteristic visible spectrum [20]. The thiocyanate compound was further characterized by infrared spectroscopy (ν SCN) = 2137 cm^{-1}).

Table 1. Products from the reaction of $[NiX_2(PPh_3)_2]$ with sulphur.

Colour of $[NiX_2]$	X	% Yield of $SPPh_3$^{a}
Pale green	Cl	89
Cream	Br	91
Black	I	76
Pale yellow	NCS	82
Pale green	NO_3	85

^{a} Because of the solubility of $SPPh_3$ in CH_2Cl_2 and hexane it was difficult to obtain quantitative yields of $SPPh_3$.

Table 2. ^{1}H NMR data.

Compound	^{1}H NMR ($CDCl_3$), ppm
[NiCl(PPh_3)(dtc)]	7.78 - 7.23 (5H, m)^b 3.62 - 3.44 (2H, m) 1.29 - 1.05 (3H, m)
[Ni($dtc)_2$]	3.71 - 3.44 (2H, q) 1.29 - 1.11 (3H, t)
$SPPh_3$	7.85 - 7.31 (5H, m)

^{b}m = multiplet, t = triplet, and q = quartet.

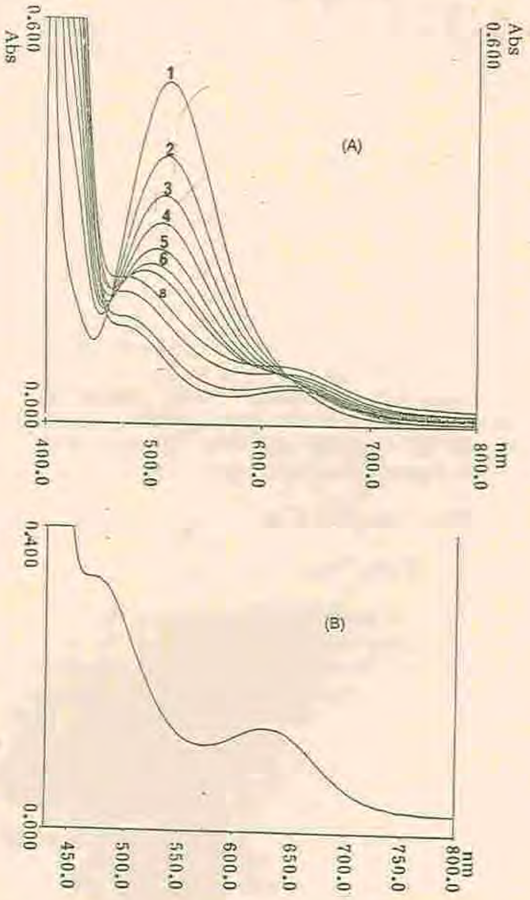


Fig. 1. Visible spectra of the reaction of NiCl(PPH_3)(dtc) with sulphur showing time in minutes after which spectra were recorded: (A) 1=0, 2=15, 3=30, 4=45, 5=60, 6=120, 7=180, 8=240, 9=300, 10=360, 11=420. (B): spectrum after 18 hours.

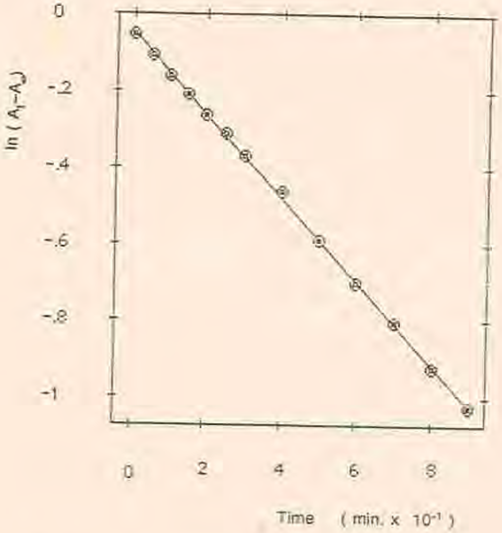


Fig. 2. First-order plot for the reaction of NiCl(PPh_3)(dtc) with sulphur at 30.5 °C for the first 90 minutes of reaction time.

When the filtrates were reduced in volume to about 10 ml and hexane was added, white crystals of $SPPh_3$ were obtained on cooling to -15°C. The yield of $SPPh_3$ from each of the reactions is shown in Table 1. This product was identified by ^1H NMR (Table 2), infrared spectroscopy [21] and elemental analysis. The reaction of NiCl(PPh_3)(dtc) with sulphur is much slower than those of $NiX_2(PPh_3)_2$. There was no visible colour change on refluxing until 1 hr of refluxing time had elapsed. It was much slower at room temperature and required more than 24 hrs for complete reaction. Under reflux conditions, reaction was complete within 4 hrs and proceeded according to equation (2).

$$NiCl(PPh_3)(dtc) + 1/8\ S_8 \rightarrow NiCl_2 + Ni(dtc)_2 + SPPh_3 \qquad (2)$$

The precipitate of $NiCl_2$ was identified by UV/vis spectroscopy as described above.

Green $Ni(dtc)_2$ and colourless $SPPh_3$ were isolated from the filtrate. $Ni(dtc)_2$ can be distinguished from NiCl(PPh_3)(dtc) by ^1H NMR (Table 2); its infrared and visible spectra were identical to those of a sample prepared by the literature procedure [22]. $SPPh_3$ was identified as discussed above.

In an attempt to detect intermediate products, reaction 2 was monitored by UV/vis spectroscopy in the 400-800 nm region at 15 and 60 min intervals. When excess sulphur was used at room temperature, the visible spectrum of NiCl(PPh_3)(dtc) gradually changed to that of $Ni(dtc)_2$ (Fig. 1). No intermediate products were detected.

A kinetic study of reaction 2 for the first 90 min indicated that the disappearance of NiCl(PPh_3)(dtc) follows first-order kinetics. A plot of ln (A_t-A_∞) vs time was linear (Fig. 2), with a rate constant of 10.8×10^3 min^{-1}. The observed rate is much slower than that observed by Bartlett and Meguerian [23] for the reaction of PPh_3 and sulphur, which proceeds with second order kinetics. This information and the fact that NiCl(PPh_3)(dtc) solutions in dichloromethane are stable at room temperature for at least one week, preclude a direct reaction of dissociated PPh_3 with sulphur. The nickel complex itself is directly involved in the formation of $SPPh_3$. This implies that the sulphur initially coordinates to the nickel center, which then rearranges to give the products (Scheme 1).

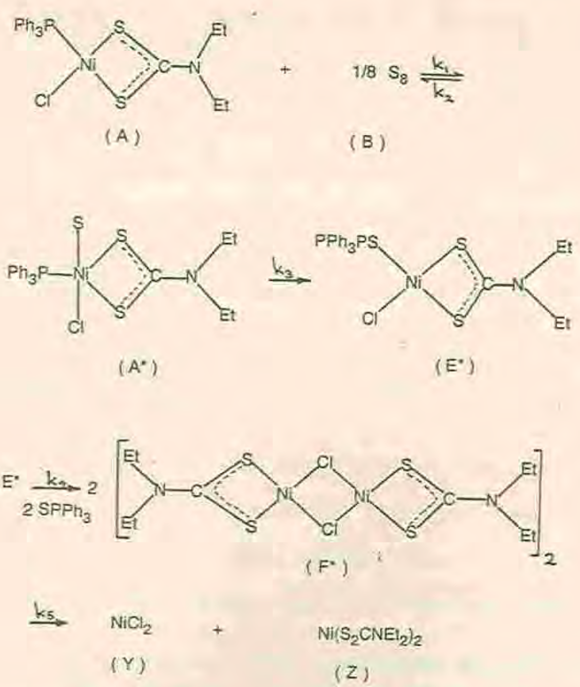
We can represent the various steps in the proposed mechanism as:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^* + B \qquad (3)$$

$$A^* \xrightarrow{k_3} E^* + SPPh_3 \qquad (4)$$

$$E^* + E^* \xrightarrow{k_4} F^* \qquad (5)$$

$$F^* \xrightarrow{k_5} Y + Z \qquad (6)$$



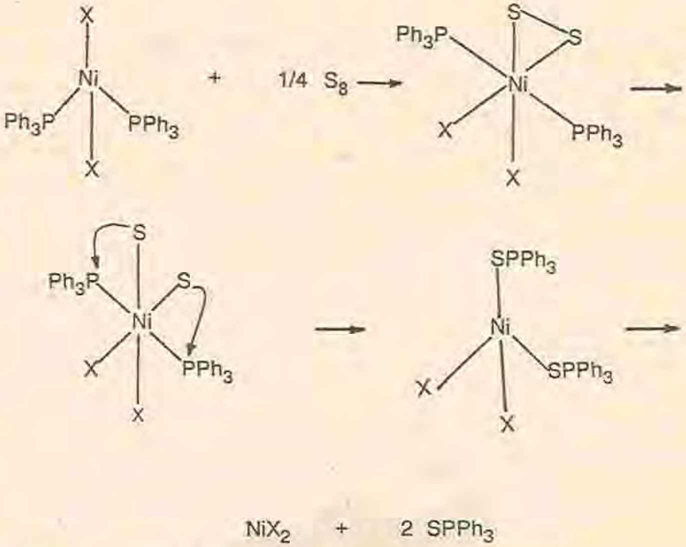
Scheme 1: Proposed pathway for the reaction of $NiCl(PPh_3)(S_2CNEt_2)$ with sulphur.

Since the sulphur is in excess, we expect some of it to remain, even when A* is formed. The intermediate A* would rearrange to form a phosphine sulphide complex which would dissociate to $SPPh_3$ and E*. We also expect the 14 electron complex, E*, to be highly unstable and to dimerize rapidly to F*. Dimer F* forms Y and Z *via* rearrangement. Applying a steady state approximation to the formation of A*, E* and F* leads to equation 7 where P represents the product.

$$\frac{d[P]}{dt} = \frac{k_3 k_1 [A][B]}{k_2[B] + k_3} \qquad (7)$$

The observed first order kinetics with respect to the initial reactant, A, indicates that $k_2[B] >> k_3$. The observed first-order rate constant is then $k_3k_1/k_2 = 10.8 \times 10^{-3}$ min^{-1} at 30.5°C for the initial 90 min of the reaction. $NiX_2(PPh_3)_2$ would also react with sulphur through initial coordination of sulphur as proposed in Scheme 2. The non-observance of any intermediates in these reactions is evidently due to fast transformations of any such intermediates. This corresponds to the inital coordination of sulphur as the rate determining step.

$Ni[SP(CH_3)_2N(CH_3)_2PS]_2$ and $NiX_2[SP(Ph_2)CH_2(Ph_2)PS]$ (X = Br, and I) [24-26], contain phosphorous-sulphur ligands. These complexes are similar to our proposed intermediates and are also similar to $[Ni(OPPh_3)(SCN)Cl]_2$, obtained when coordinated PPh_3 in $Ni(PPh_3)_2(SCN)_2$ is oxidized by NOCl [27]. Loss of the coordinated $SPPh_3$ in our proposed mechanism, should be quite facile since phosphine sulphides, unlike phosphine oxides, have weak donor properties towards nickel(II) [22].



Scheme 2: Proposed pathway for the formation of $SPPh_3$ and NiX_2.

Similar loss of PPh_3 as $SPPh_3$ when ruthenium [28] and palladium [29] phosphine complexes react with sulphur has also been recently reported. Our observation of the loss of PPh_3 when $NiCl(PPh_3)(dtc)$ is reacted with thiols [30] makes loss of the weaker ligand, $SPPh_3$, even more plausible. The results of our study point to the potential of $NiX_2(PPh_3)_2$ and $NiCl(PPh_3)(dtc)$ as desulphurization reagents. We are currently exploring this possibility.

ACKNOWLEDGEMENTS

This research was supported by grants from the University of Zimbabwe and the university of Botswana (to J.D.)., and from Gettysburg College through an Institutional Self-Renewal grant (to L.M.K.). Initial experimental assistance by Margaret Machingambi and Sam Manyella, University of Zimbabwe, is gratefully acknowledged.

REFERENCES

1. O.Weisser and S. Landa, "Sulfide Catalysts, their Properties and Applications," Pergamon Press, New York (1983).
2. W.H. Pan, D.C. Johnson, S.T. Mckenna, R.R. Chiannelli, T.R. Halbert L.L. Hutchings and E.I. Stiefel, Inorg. Chim. Acta, **97**, L17 (1985).
3. M.S. Whittingham, Prog. Solid State Chem., **12**, 41 (1978).
4. J.A. Ibers and R.H. Holm, Science, **200**, 223 (1980).
5. M. Teixeira, I. Moura, A.V. Xavier, D.V. DerVartanian, J. LeGall, H.D. Peck Jr., B.H. Huynh, and J.J.G. Moura, Eurp. J. Biochem., **130**, 481 (1983).
6. J.J. Eisch, L.E. Hallenbeck, and K.I. Han, J. Amer. Chem. Soc., **108**, 7763 (1986).
7. S. Becker, Y. Fort, R. Vanderesse and P. Caubere, J. Org. Chem., **54**, 4848 (1989).
8. P.W. Jolly, "Comprehensive Organometallic Chemistry", G. Wilkinson Eds. Pergamon Press, New York, **6**, 9 (1982).
9. H. Vahrenkamp, V.A. Uchman and L.F. Dahl, J. Amer. Chem. Soc., **90**, 3272 (1969).
10. C.A. Ghilardi, S. Midollini and L. Sacconi, J. Chem. Soc. Chem. Commun., **47** (1981).
11. C.A. Ghilardi, S. Midollini and L. Sacconi, Inorg. Chim. Acta, **31**, L431 (1978).
12. D. Fenske, A. Hollnagel and K. Merzweiler, Angew. Chem., **100**, 978 (1988).
13. S. Akabori, T. Kumagai, T. Shirahige, S. Sato, K. Kawazoe, C. Tamura, and M. Sato, Organometallics, **6**, 2105 (1987).
14. C.E. Briant, G.R. Hughes, P.C. Minshall and D.M.P. Mingos, J. Organomet. Chem., **202**, C18 (1980).
15. C.E. Briant, M.J. Calhorda, T.S.A. Hor, N.D. Howells and D.M.P. Mingos, J. Chem. Soc. Dalton Trans., 1325 (1983).
16. J. Chatt and D.M.P. Mingos, J. Chem. Soc., 1243 (1970).
17. J. Venanzi, J. Chem. Soc., 719 (1958).
18. P.L. Maxfield, Inorg. Nucl. Chem. Lett., **6**, 693 (1970).
19. Programme written by Donald Dahlberg, Lebanon College, Annville, PA, U.S.A.
20. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 5th Ed., John Wiley, New York, 744 (1988).
21. The infrared spectrum of the $SPPh_3$ isolated from each of the reactions was identical to that found in the literature: C.J. Pouchert, Aldrich Library of infrared Spectra, 2nd Ed., (1978), p 1037.
22. L. Sacconi, F. Mani and A. Bencini in "Comprehensive Coordination Chemistry" G. Wilkinson, R.D. Gillard and J.A. McCleverty Eds., Pergamon Press, Oxford **5**, 185 (1987).
23. P.D. Bartllet and G. Meguerian, J. Amer. Chem. Soc., **78**, 3710 (1956).
24. M.R. Churchill, J. Cooke, J.P. Fennessey and J. Wormald, Inorg. Chem., **10**, 1031 (1971).
25. A. Davidson and E.S. Switkes, Inorg. Chem., **10**, 837 (1971).
26. W.E. Slinkard and D.W. Meek, J. Chem. Soc. Dalton Trans., 1024 (1973).
27. K.P. Sarma and R.J. Poddar, Transition Met. Chem., **8**, 31 (1983).
28. D. Sellman and I. Barth, Inorg. Chim. Acta, **164**, 171 (1989).
29. B. Grociani, F.D. Bianca, M. Consiglio, M. Paci and P. Tagliatesta, Inorg. Chim. Acta, **167**, 171 (1990).
30. J. Darkwa and L.M. Koczon, unpublished results.