A Double CS_2-bridged Nickel Complex. New Synthesis and Crystal Structure of $[(PPh_3)Ni(\mu\text{-}CS_2)_2Ni(PPh_3)]$

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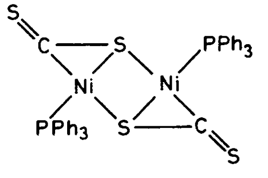
The reaction of $[(PPh_3)_2Ni(C_3Ph_3)]BPh_4$ with CS_2 gives $[(PPh_3)Ni(\mu\text{-}CS_2)]_2$, whose molecular structure, determined by an *X*-ray analysis, consists of dimeric centrosymmetric molecules in which the metal atoms are held together by two bridging CS_2 groups.

In 1967 Wilkinson[1] treated the complex $[(PPh_3)Ni(CO_2)]$ with carbon disulphide to obtain deep red crystals of empirical formula $[(PPh_3)Ni(CS_2)]$. On the basis of i.r. data and molecular weight measurements, it was tentatively assigned structure (**1**). Other researchers, namely Uhlig[2] and Ibers,[3] later synthesized complexes of the formula $[(PPh_3)Ni(CS_2)]$ by the respective reactions of CS_2 with $[(PPh_3)_2Ni(C_2H_4)]$ or $Ni(cod)_2$ (cod = cyclo-octa-1,5-diene) in the presence of PPh_3. In either case no crystals suitable for an *X*-ray analysis were obtained. However, both of these complexes were assigned the proposed structure (**1**). The structure of the complex (**1**) is still an unresolved problem in CS_2 co-ordination chemistry. We treated a methylene chloride solution of the cyclopropenyl complex $[(PPh_3)_2Ni(C_3Ph_3)]BPh_4$[4] with gaseous CS_2, at room temperature and isolated deep red crystals of a diamagnetic complex analysed as $[(PPh_3)Ni(CS_2)]$ (30% yield). Its molecular structure was then established by a single-crystal *X*-ray analysis.

Crystal data: $C_{38}H_{30}Ni_2P_2S_2$, $M = 794.28$, triclinic, space group $P\bar{1}$, $a = 10.490(6)$, $b = 9.892(5)$, $c = 9.509(5)$ Å, $\alpha = 64.17(6)$, $\beta = 87.12(7)$, $\gamma = 86.00(6)°$, $U = 885.80$ Å^3, $Z = 1$, $D_c = 1.489$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 14.10$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å.

Intensity data were collected on a Philips PW 1100 automatic diffractometer using the ω–2θ scan technique and graphite monochromated Mo-K_α radiation. The structure, solved by the heavy atom method, was refined using full-matrix least-squares. Throughout the refinement the phenyl rings were treated as rigid bodies. The final R and R_w values are 0.054 and 0.048 respectively for 833 observed reflections ($2\theta \leqslant 50°$) having $I \geqslant 3\sigma(I)$.[†]

The molecular structure consists of dimeric molecules $[(PPh_3)Ni(\mu\text{-}CS_2)_2Ni(PPh_3)]$, whose perspective view is shown in Figure 1. The two $Ni(PPh_3)$ fragments, which are related by a crystallographic inversion centre, are held together by two CS_2 molecules so that a six-membered ring is formed. Each CS_2 molecule is π-bonded through the C=S linkage to one metal atom and σ-bonded to the other nickel through the second sulphur atom. The co-ordination around each nickel atom is distorted square planar, the distortion being mainly due to the short bite of the C=S linkage [C–Ni–S(2) 47.5(5)°] and to the requirement of the six-membered ring. The metal atom is 0.044 Å out of the least-squares plane defined by the four ligands and 4.079(3) Å from the other symmetry-related metal atom. The lengthening of the C–S(1) bond distance [1.68(1) Å] with respect to the monomeric η^2-CS_2 complex $[(tppme)Ni(CS_2)]$[5,6] [tppme = $MeC(CH_2PPh_2)_3$, C–S(1) 1.61(1) Å], is not unexpected, and also occurs in other CS_2 dimeric complexes where only one CS_2 group bridges two metal centres.[7,8] However, the planarity of the $Ni(\mu\text{-}CS_2)_2Ni$ entity (largest deviation from the mean plane 0.034 Å) suggests the possibility of an overall electronic delocalization, which is probably responsible for the stability of this compound.



(1)

Since the i.r. spectrum of our complex $[(PPh_3)Ni(CS_2)]_2$[‡] is

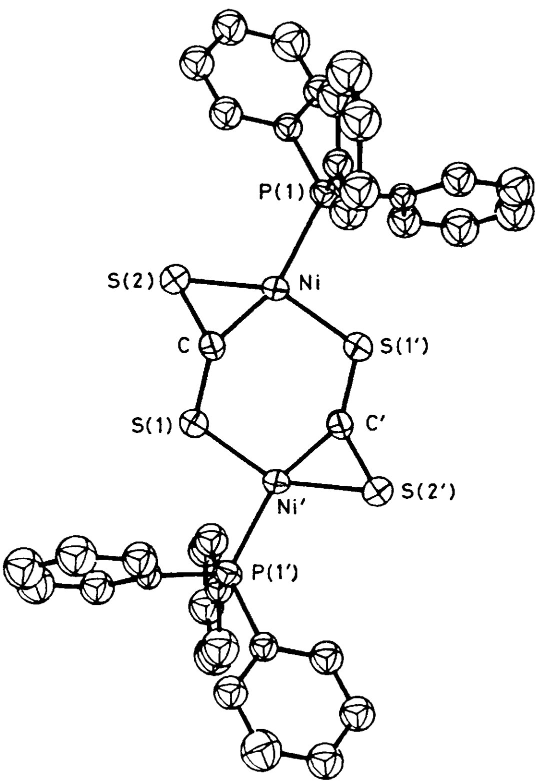
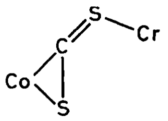


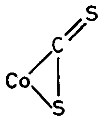
Figure 1. Perspective view of the complex $[(PPh_3)Ni(\mu\text{-}CS_2)]_2$. ORTEP drawing with 50% probability ellipsoids. Selected bond distances and bond angles: Ni–P(1) 2.232(4), Ni–S(2) 2.157(4), Ni–S(1′) 2.150(4), Ni–C 1.81(1), S(1)–C 1.68(1), S(2)–C 1.63(1), Ni · · · Ni′ 4.079(3) Å; P(1)–Ni–S(2) 112.5(2), P(1)–Ni–S(1′) 97.2(2), P(1)–Ni–C 159.0(4), S(2)-Ni-S(1′) 150.3(2), S(2)–Ni–C 47.5(5), S(1′)–Ni–C 103.0(4), Ni–S(1′)–C′ 111.9(5), Ni–C–S(1) 145.0(9), S(1)–C–S(2) 137.3(9)°.

[†] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[‡] I.r. (Nujol): 1590(vw), 1483(s), 1438(vs), 1310(vw), 1200(vw), 1183(w), 1170(m), 1125(vs), 1097(s), 1070(vw), 1027(w), 998(w), 970(vw), 916(vw), 850(vw), 744(s), 717(s), 704(m), 690(vs), 540(m), 522(vs), 500(s), 440(w), 420(w) cm^{-1}.



(2)



(3)

completely superimposable on that of the complex previously reported by Wilkinson, we probably have the same compound.

A strong i.r. band at 1122 cm^{-1} could indicate[1] an uncoordinated C=S linkage. However, we have recently found that frequencies in the range 1110—1160 cm^{-1} are also typical of μ-CS_2 complexes, where the bonding mode of carbon disulphide is analogous to that found in our complex $[(PPh_3)Ni(CS_2)]_2$. In particular, the dinuclear complex $[(tppme)Co(\mu\text{-}CS_2)Cr(CO)_5]$[8] (2) has a ν(CS) at 1110 cm^{-1}, whereas the mononuclear parent complex $[(tppme)Co(\eta^2\text{-}CS_2)]$[8] (3) has a band at 1120 cm^{-1}. Since the complex $[(tppme)Ni(\eta^2\text{-}CS_2)]$[5] exhibits a band at 1145 cm^{-1}, a shift of 23 cm^{-1} in the ν(CS) stretching frequency is not unexpected for our compound $[(PPh_3)Ni(CS_2)]_2$. Finally, the i.r. spectrum does not show any band near 600 cm^{-1} attributable to $\overline{\mathrm{M{-}C{-}S}}$ ring vibrations.

Received, 30th March 1983; Com. 417

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