549. *Studies in Co-ordination Chemistry. Part XII.* A Ditertiary Arsine Nickel Carbonyl and Some Halogen Derivatives.*

By R. S. NYHOLM.

The reaction between nickel tetracarbonyl and the ditertiary arsine chelate group, *o*-phenylenebisdimethylarsine, has been studied. Two carbonyl groups are replaced readily to yield a stable crystalline compound of the formula $Ni(CO)_2$Diarsine, which is diamagnetic and monomeric in freezing benzene. Attempts to replace all four carbonyl groups were unsuccessful. Oxidation of the complex with iodine liberates the carbon monoxide, giving the compound NiI_2Diarsine, first of a previously unknown class of *cis*-planar bivalent nickel complexes. This substance is red and diamagnetic; it is monomeric in freezing ethylene dibromide and is a non-electrolyte in nitrobenzene. The corresponding bromide and chloride are much less stable. The further oxidation of these compounds has been investigated and a tervalent nickel complex bromide of the formula $NiBr_3$Diarsine is described.

IN an attempt to prepare the bis(ditertiary arsine)–nickel^0 complex (III), the behaviour of the chelate group *o*-phenylenebisdimethylarsine (I) with nickel carbonyl has been studied. It has already been shown that this chelate group stabilises bi-, ter-, and quadrivalent nickel in various complexes (*J.*, 1950, 2061; 1951, 2602) and it was hoped that this chelate group might be more effective than trialkylphosphines and trialkylarsines for the replacement of all four carbonyl (CO) groups. Most ligands which react directly with nickel carbonyl replace two carbonyl groups only. Thus by direct replacement the following compounds, for example, may be prepared: $Ni(CO)_2$Dipyridyl; $Ni(CO)_2$*o*-Phenanthroline; $Ni(CO)_2$(Triphenylphosphine)$_2$. The last is a white crystalline compound, m. p. 192°, whilst the first two are red [for detailed summary see "Acetylene and Carbon Monoxide Chemistry" by Copenhaver and Bigelow, Reinhold Publ. Corpn., N.Y., 1949, pp. 260, 297; also Hieber and Bockly, *Z. anorg. Chem.*, 1950, **262**, 344, and Hein, "Chemische Koordinationslehre," Zurich, 1950, p. 347]. By using alkyl and aryl cyanides more than two carbonyl groups may be replaced; thus, Hieber (*Z. Naturforsch.*, 1950, **5**, *B*, 129) has prepared the compounds $Ni(C{\equiv}N{-}C_6H_5)_4$ and $Ni(C{\equiv}N{-}CH_3)_3CO$. Using similar methods, Wilkinson (*Nature*, 1951, **168**, 514) has recently prepared the compounds $Ni(PF_3)_4$ and $Ni(PCl_3)_4$. Chatt (*J.*, 1951, 3061) has shown that phosphorus trifluoride does not react directly with metallic nickel but on its prolonged refluxing with nickel carbonyl at least three carbonyl groups are replaced, giving a liquid product. These phosphorus trihalide compounds suffer from the disadvantage that they are readily hydrolysed and it is therefore of interest to obtain less reactive compounds for physical investigations.

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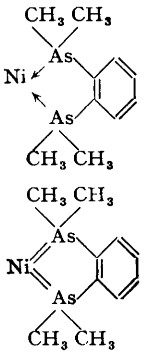
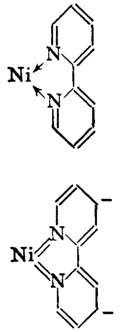
* Part XI, *J.*, 1952, 1257.

It seems most significant that the groups which add to zerovalent nickel are just those for which double-bond structures may be written. The formulation of $Ni(CO)_4$ with four co-ordinate links (σ-bonds) would leave the nickel atom with a most improbable negative charge. This may be decreased by using some of the $3d$ electron pairs of the nickel atom for double (π) bonding with a suitable vacant orbital of the ligand; this would need to be a p orbital in the case of a first-row element or a d orbital for second- or later-row elements of the periodic table (for summary references see Part X, *J.*, 1951, 3245). The possible number of strong double bonds in a tetrahedral complex is two (Kimball, *J. Chem. Phys.*, 1940, **8**, 194) and, since there are more than sufficient $3d$ electron pairs on the nickel atom to permit this, double bonding probably takes place to a marked extent in all cases; some evidence in support of this view is given below. The contributory structures to the resonance hybrid in certain cases are shown below.

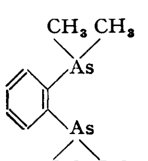
$\mathrm{Ni{\leftarrow}C{\equiv}O} \qquad \mathrm{Ni{\leftarrow}C{\equiv}N{-}R} \qquad \mathrm{Ni{\leftarrow}PR_3}$

$\mathrm{Ni{=}C{=}O} \qquad \mathrm{Ni{=}C{=}N{-}R} \qquad \mathrm{Ni{=}PR_3}$

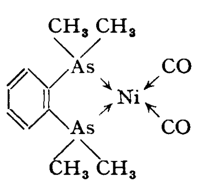




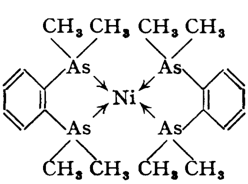
It has been found that, while the ditertiary arsine replaces two carbonyl groups with extreme ease, the remaining two are much less reactive. When nickel carbonyl is heated under reflux with the ditertiary arsine dissolved in benzene or light petroleum, carbon monoxide is evolved and on removal of the solvent compound (II) only is isolated; varying the proportions of the two reactants did not alter the product. Furthermore, even when (II) is heated at 200° with excess of the chelating compound in the presence of hydrogen, decomposition rather than replacement occurs. Compound (II), *o*-phenylenebisdimethylarsinedicarbonylnickel^0, was isolated as colourless crystals, m. p. 125°, which are readily soluble in all solvents tried except water. It is very soluble in benzene in which it is monomeric at the freezing point, showing that the nickel atom is four-covalent. The compound is diamagnetic, like the parent tetracarbonyl, suggesting that the bonds are $4s4p^3$ and hence that the nickel atom is tetrahedral. Electric dipole moment data would not assist in determining the stereochemistry since both a planar and a tetrahedral arrangement of the four bonds would result in a finite dipole moment of approximately the same value; however, there is no reason for believing that the four bonds are planar. The difficulty of removing the two remaining carbonyl groups suggests at first sight that these are more strongly bound than in nickel carbonyl itself. A comparison of the force constants



(I)



(II)



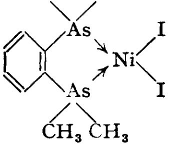
(III)

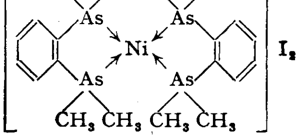
of the C–O bonds in $Ni(CO)_2$Diarsine and in $Ni(CO)_4$, however, shows that there is little change in the C–O bond order in the two compounds and hence presumably the bond order of the Ni–C bond is approximately the same in both cases (unpublished infra-red studies by

Nyholm and Short). The difficulty of removing the remaining two carbonyl groups thus appears to arise from mechanistic difficulties rather than from any increase in the strength of binding of these two groups compared with the four in Ni(CO)$_4$. Attempts to obtain compound (III) by heating finely powdered nickel with the ditertiary arsine were also unsuccessful.

A solution of (II) in alcohol undergoes a striking series of colour changes when treated with chlorine in carbon tetrachloride. The colourless solution first becomes red, a colour which is usually indicative of the presence of a diamagnetic bivalent nickel complex; on further addition of chlorine the solution becomes yellow and finally develops an emerald-green colour. Yellow and green colours have been observed previously when ter- and quadri-valent nickel complexes are present in aqueous solution, and the reaction with halogens was therefore studied in more detail. When compound (II) in benzene solution is treated with one molecular proportion of iodine, a deep red colour appears at once and a vigorous effervescence occurs. A beautiful crimson precipitate with the empirical formula NiI$_2$Diarsine is obtained. This compound is readily soluble in nitrobenzene to a red solution; the molecular conductivity in this solvent in M/1000-concentration is less than 1 mho, indicating that the compound is a non-electrolyte since uni-univalent electrolytes have molecular conductivities of the order of 20—30 mho in this solvent at this concentration (see Part VII, *J.*, 1951, 38). In freezing ethylene dibromide the compound is monomeric, showing that the nickel atom is four-covalent and hence confirming the formulation shown in (IV). The planar arrangement of the four bonds may be inferred from the fact that the compound is diamagnetic, the latter indicating that the bonds are $3d4s4p^2$. In Part V (*J.*, 1950, 2061) attempts to make the corresponding chloro-compound by the direct action of the ditertiary arsine on nickel chloride in alcoholic solution were described. On that occasion only the bis(ditertiary arsine) complex similar to (V) could be isolated. When the compound [Ni(Diarsine)$_2$]Cl$_2$ was refluxed for many hours with excess of nickel chloride in an inert atmosphere no change was apparent; it was concluded that in alcoholic solution the compound NiCl$_2$Diarsine was unstable with respect to [Ni(Diarsine)$_2$]Cl$_2$ and nickel chloride. Owing to the insolubility of the compounds [Ni(Diarsine)$_2$]Br$_2$ and [Ni(Diarsine)$_2$]I$_2$ in alcohol the preparation of [Ni(Diarsine)Br$_2$]^0 and [Ni(Diarsine)I$_2$]^0 by this method was not attempted. The ease with which (II) passes over into the *salt* [Ni(Diarsine)$_2$]I$_2$ (V) is shown by the fact that when a solution of (II) in nitrobenzene, chloroform, etc., is treated with the ditertiary arsine the red colour is discharged instantly and a brown precipitate of the salt is obtained.

Attempts to prepare the pure bromide and chloride corresponding to (IV) were less successful. Addition of the requisite amount of bromine to (II) in benzene gave a reddish-brown precipitate which gave analytical figures only approximately correct for NiBr$_2$Diarsine. Extraction with chloroform gave a small yield of the required complex as a pink powder with properties similar to those of (IV). The complex could not be obtained pure and this is reflected both in the analysis and in weak paramagnetism. When kept the compound quickly became brown owing to decomposition. The chloro-compounds were even less stable than the iodide and bromide, and no compound corresponding with the formula NiCl$_2$Diarsine could be isolated. Compounds of the general formula Ni(Hal)$_2$Diarsine thus become progressively more difficult to obtain pure as the halogen atom becomes more electronegative. Two reasons can be suggested to explain this experimental difficulty. First, it is known for Ni(II) complexes that, as the electronegativity of the attached groups increases, there is an increasing tendency to utilise orbitals higher than the planar $3d4s4p^2$ orbitals and hence a change over from the planar diamagnetic to the


(IV)


(V)

tetrahedral paramagnetic complexes occurs. Thus, whereas $NiCl_2,2(C_2H_5)_3P$ is red and diamagnetic, $Ni(NO_3)_2,2(C_2H_5)_3P$ is green and paramagnetic with a tetrahedral configuration. These tetrahedral complexes tend to pass over to octahedral ones very easily, and hence attack on the molecule and subsequent decomposition is facilitated (Nyholm, *Quart. Reviews*, 1949, **3**, 321). The second possible explanation arises from the fact that these complexes would have a *cis*-planar arrangement and it is known that at least with Pt(II) complexes of tertiary arsines the reactivity of the *cis*-isomer is greater than that of the *trans* (see Part I, *J.*, 1950, 843). Finally, it is relevant to mention that using triethylarsine, Jensen (*Z. anorg. Chem.*, 1936, **229**, 265) was able to isolate the iodide $NiI_2,2(C_2H_5)_3As$ but neither the bromide nor the chloride.

The compound NiI_2Diarsine is the nickel analogue of the palladium complex $PdCl_2$Diarsine described by Chatt and Mann (*J.*, 1939, 1622). As far as is known, this is the first definite example of a *cis*-planar chelated complex of bivalent nickel. Chatt and Mann (*loc. cit.*) found that the palladium complex, like the nickel compound, was only slightly soluble in most solvents except chloroform.

The action of excess of halogen on compound (II) has also been investigated. When (II) is treated with a slight excess of bromine a brownish-black compound is precipitated, the empirical formula of which is $NiBr_3$Diarsine. The magnetic moment of this substance (2·4 B.M.) indicates that the nickel atom is tervalent. Owing to the insolubility of the compound in organic solvents its molecular complexity could not be determined. This insolubility suggests that polymerisation occurs to give a six-covalent Ni(III) complex, and formulation as a five-covalent non-electrolyte similar to $NiBr_3,2(C_2H_5)_3P$ (Jensen, *loc. cit.*) seems much less likely. The compound may be reduced by sulphur dioxide in acetone suspension, to yield the pink bivalent complex again. Attempts to obtain a nickel complex with a higher bromine content led to products of indefinite composition. Addition of excess of iodine to compound (II) gives black crystals of the formula NiI_4Diarsine. These are diamagnetic, but whether the nickel atom is bi- or quadri-valent is unknown since the compound may well be a polyiodide. Owing to its insolubility it was not further investigated.

The relations between the various complexes are summarised in the chart.

$$\begin{tikzcd}
Ni(CO)_4 \arrow[r, "\text{Diarsine}"] & Ni(CO)_2\text{Diarsine} \arrow[r, "Br_2 \text{ in } C_6H_6"] \arrow[d, "I_2 \text{ in } C_6H_6"] & {[NiBr_2\text{Diarsine}]^0} \arrow[r, "\text{Excess of } Br_2"] & NiBr_3\text{Diarsine} \\
{[Ni(\text{Diarsine})_2]I_2} & {[NiI_2\text{Diarsine}]^0} \arrow[l, "\text{Diarsine}"'] \arrow[r, "I_2"] & NiI_4\text{Diarsine} &
\end{tikzcd}$$

EXPERIMENTAL

o-Phenylenebisdimethylarsinedicarbonylnickel^0.—Nickel tetracarbonyl (1·5 g.), dissolved in benzene (7 ml.), was treated with the ditertiary arsine (2·0 g.) dissolved in light petroleum (5·0 ml.; b. p. 60—80°), and the solution heated under reflux in an atmosphere of carbon dioxide. The colourless solution gradually became yellow and after 1 hour was deep brown, some nickel being in suspension. The solution was filtered and the pale yellow filtrate was allowed to evaporate spontaneously. The almost colourless crystalline *complex* was recrystallised from the minimum volume of alcohol, yielding large colourless crystals (1·2 g.), m. p. 125° (Found: C, 36·0; H, 4·0; Ni, 14·75. $C_{12}H_{16}O_2As_2Ni$ requires C, 35·9; H, 4·0; Ni, 14·65%). The compound is readily soluble in non-hydroxylic solvents, moderately soluble in alcohol, but insoluble in water. In aqueous alcohol it is slowly hydrolysed, a green precipitate of nickel hydroxide being formed. The molecular weight (cryoscopic in 3·83% benzene solution) was 380 (Required: 400·7). Magnetic susceptibility: in powder form the compound is diamagnetic with $\chi_g = -0{\cdot}28 \times 10^{-6}$ at 17·5°.

o-Phenylenebisdimethylarsinedi-iodonickel^{II}.—The above dicarbonyl complex, $Ni(CO)_2$Diarsine (0·40 g.), dissolved in cold benzene (8 ml.), was treated with iodine (0·25 g.) in warm benzene (20 ml.); the solution became purplish red, a red precipitate being formed. During the reaction a vigorous effervescence occurred, carbon monoxide being evolved. After cooling, the *compound* (0·62 g.) was filtered off and well washed with benzene before being dried *in vacuo* (Found: C, 19·8; H, 2·85; I, 41·5; Ni, 9·67. $C_{10}H_{16}As_2I_2Ni$ requires C, 20·0; H, 2·7; I, 42·4; Ni, 9·79%). The substance dissolves in acetone, chloroform, or nitrobenzene, and is moderately soluble in benzene, but practically insoluble in alcohol and insoluble in water or light petroleum. It is decomposed by water, yielding a brown residue, presumably the salt $[Ni(Diarsine)_2]I_2$ since the filtrate from the latter contains nickel ions resulting from disproportionation. When a chloroform solution is treated with the ditertiary arsine the reddish-purple colour is discharged instantly, the brown salt $[Ni(Diarsine)_2]I_2$ being precipitated. When heated, the compound changes colour and melts with decomposition at *ca.* 140°. The compound is diamagnetic in the powder form with $\chi_g = -0{\cdot}15 \times 10^{-6}$. In nitrobenzene the complex is a non-electrolyte, the molecular conductivity in $0{\cdot}8 \times 10^{-3}$M-solution being 0·8 mho The molecular weight (cryoscopic in 0·55% ethylene dibromide solution) is 580 (Required : 599).

Action of Bromine on $Ni(CO)_2$Diarsine.—The dicarbonyl nickel complex was treated with bromine (*a*) in the ratio Br : Ni = 2 : 1 and (*b*) in excesss.

(*a*) To the dicarbonyl compound (0·5 g.) in sodium-dried *cyclo*hexane (25 ml.) was added bromine (0·2 g.) in carbon tetrachloride (10 ml.), with vigorous stirring to avoid the formation of local concentrations of bromine leading to the tribromide. A reddish to red-brown precipitate (0·65 g.) was obtained which was filtered off and well washed with *cyclo*hexane and dried *in vacuo.* This compound was paramagnetic ($\chi_g = +0{\cdot}5 \times 10^{-6}$) and hence was not pure dibromide. It was treated with chloroform (50 ml.), the whole was filtered, and the filtrate treated with light petroleum, yielding a pink powder (0·2 g.). This was still very weakly paramagnetic and hence not pure. Analysis (C, 22·6; H, 4·7; Br, 28·2; Ni, 10·2. Calc. for $C_{10}H_{16}As_2Br_2Ni$: C, 23·7; H, 3·2; Br, 31·7; Ni, 11·6%) confirms that the compound is impure but all attempts to obtain the pure complex were unsuccessful. The compound became brown within 24 hours. When benzene was used, the initial precipitate had a beautiful crimson colour but during isolation the compound became brown and its analytical figures were poor.

(*b*) The carbonyl complex, $Ni(CO)_2$Diarsine (0·4 g.), in dry *cyclo*hexane (40 ml.) was treated with bromine (0·24 g.) in carbon tetrachloride (12·5 ml.), the mixture being well stirred during and after the addition. The dark brown precipitate (0·45 g.) was filtered off, well washed with *cyclo*hexane, and dried *in vacuo* (Found : C, 19·3; H, 3·2; Br, 40·2. Calc. for $C_{10}H_{16}As_2Br_3Ni$: C, 20·5; H, 2·73; Br, 41·0%). The complex was thus not the pure tribromide but further attempts to obtain a less impure product gave substances with variable analyses. The reason for this is probably that the bromination of the solid bivalent compound is incomplete and that partial decomposition may occur. The compound was insoluble in organic solvents and decomposed when kept. When the compound was treated in acetone suspension with sulphur dioxide a pink colour developed, presumably owing to reduction. Magnetic susceptibility : $\chi_g = 3{\cdot}4 \times 10^{-6}$, $\chi_M = 1990 \times 10^{-6}$, diamagnetic correction = 285×10^{-6}, whence $\mu = 2{\cdot}4$ B.M. The impurity is thus also reflected in the magnetic moment which is unusually high for one unpaired electron.

Action of Iodine on NiI_2Diarsine.—The di-iodo-complex (0·1 g.) in ethylene dibromide (14 ml.) was filtered from traces of insoluble material formed on storage and treated with iodine (0·07 g.) dissolved in ethylene dibromide (5 ml.). The purplish-red solution of the di-iodide became very much darker and black crystals appeared. A small amount of light petroleum was added to hasten crystallisation. The *product* (0·1 g.) was filtered off and well washed with petroleum ether (Found : C, 13·8; H, 2·1; Ni, 6·7. $C_{10}H_{16}As_2I_4Ni$ requires C, 14·0; H, 1·9; Ni, 6·85%). The compound was diamagnetic showing that the nickel is either bi- or quadrivalent. Owing to the insolubility of the substance its properties were not further investigated.

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