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Stereochemistry of 5-Co-ordinated Compounds

IV. The Reaction of Nitrosyl Halides with Phosphine Complexes of Nickel and Cobalt

KAI ARNE JENSEN, BØRGE NYGAARD and CARL TH. PEDERSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen,
Copenhagen, Denmark

The phosphine complexes of nickel or cobalt of the type $[MX_2(R_3P)_2]$, where $X = Cl$ or Br, react with nitrosyl chloride or nitrosyl bromide to form complexes of the type $[MX_3(R_3P)_2]$. These compounds form intensely coloured substances, easily soluble in organic solvents. They are monomolecular in solution and have paramagnetic moments corresponding to one unpaired electron for the nickel compounds and to two unpaired electrons for the cobalt compounds. The most stable of the compounds, $[CoCl_3(Et_3P)_2]$, was found to have zero dipole moment in pentane solution. This rules out the tetragonal pyramidal configuration considered in our earlier paper [1] but is in accordance with a trigonal bipyramidal configuration for these compounds.

Whereas a complex with trivalent nickel, $[NiBr_3(Et_3P)_2]$, could be prepared by addition of bromine to a benzene solution of the corresponding complex with divalent nickel [1] the corresponding chloride could not be prepared in a similar way. Oxidation to a complex with trivalent nickel took place, as shown by the intense dark blue colour of the solution, but on evaporation of the solvent the complex was completely decomposed with the formation of nickel chloride and triethylphosphine oxide. It was, however, observed that nitrosyl chloride reacts with the compounds of the type $[NiCl_2(R_3P)_2]$ to form the corresponding trichlorides. Accordingly NO is not added, in contrast to the behaviour of platinum ammines which add nitrosyl chloride as NO^- and Cl^- to form compounds of tetravalent platinum [2]. Towards the phosphine nickel complexes nitrosyl chloride only acts as a chlorinating agent, milder than free chlorine. In this way the chloride $[NiCl_3(Et_3P)_2]$ could be prepared. It is, however, less stable than the bromide.

Nitrosyl bromide reacts in a similar way, forming with $[NiBr_2(Et_3P)_2]$ the same tribromide, which could also be prepared by means of bromine. The use of nitrosyl halides is, however, of special interest in connexion with the cobalt(II) phosphine complexes, which can not be oxidised directly to complexes with trivalent cobalt, because the ligand is oxidised. By means of nitrosyl halides compounds of the type $[CoX_3(R_3P)_2]$ can be prepared. Probably compounds of the type $[CoX_3(NO)(R_3P)_2]$ which easily split off NO are formed as intermediates in this process. Solutions of $[NiCl_3(Et_3P)_2]$ or $[CoCl_3(Et_3P)_2]$ do not absorb nitrogen oxide at room temperature, but on cooling at −80°C absorption takes place with a remarkable colour change. The dark blue solution of the nickel complex turns red-violet and the permanganate-coloured solution of the cobalt complex becomes light green. On heating to room temperature NO is again given off and the solutions regain their original colour.

Because of their potential stereochemical interest a number of such substances have been investigated with a view to finding a compound which was stable enough to allow a reliable determination of such properties as molecular weight, dipole moment, crystal structure, *etc.*

It proved, however, that the first compounds we had prepared, the compounds of triethylphosphine [3], were the most suitable, although also the tripropylphosphine compounds were quite stable and could be prepared with the correct composition. The compounds of trimethylphosphine are formed easily — in this case already by oxidation in the air — but they are less stable and could not be prepared in sufficient purity. The same applies to cobalt(III) compounds of tributyl-, triisobutyl- and tri-*sec*-butylphosphine, although it is remarkable that the tributylphosphine compound, $[CoCl_3(Bu_3P)_2]$, could be isolated in the crystalline state from $[CoCl_2(Bu_3P)_2]$, which was only isolated as an oil, *cf.* the preceding paper; its composition was, however, somewhat variable. No pure nickel(III) or cobalt(III) compounds containing tricyclohexylphosphine, triphenylphosphine, or tribenzylphosphine could be prepared. In the case of the triphenylcomplexes it seems that part of the triphenylphosphine is split off on treatment of triphenylphosphine complexes of the divalent metals with nitrosyl halides with the formation of compounds of the type $[NiCl(NO)(Ph_3P)]$ described by Feltham [4]. In the case of the tribenzylcomplexes compounds with too high content of the halogen were obtained, indicating that the benzyl group had been halogenated.

The properties of these compounds are quite remarkable. Their colour is extremely intense. The colour of the bromide $[CoBr_3(Et_3P)_2]$ resembles that of aniline blue and the chloride has almost the same colour as permanganate. The solutions of the corresponding nickel complexes have a similar intense green or blue colour; the solid compounds are almost black with a violet or green lustre. They are extremely soluble in organic solvents — with the exception of the trimethylphosphine compounds this applies even to petroleum hydrocarbons. On addition of trialkylphosphines they are slowly reduced; apparently a hexacoordinated complex is not formed (this applies also to the trimethylphosphine compounds).

On addition of bromine or nitrosyl chloride to a solution of the red halides of the type $[NiX_2(R_3P)_2]$ in benzene their spectra are changed in qualitatively the same way, the absorption maximum in ultraviolet at *ca.* 370 mμ being replaced by absorption maxima in the visible spectrum near 410 mμ and 600 mμ (Fig. 1). The absorption spectra of the cobalt(III)phosphine complexes are very similar. A closer examination of these spectra is in progress.

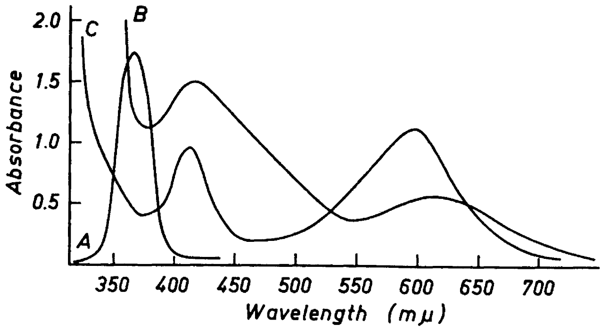

Fig. 1. Absorption spectra of a benzene solution (1 mg in 20 ml) of [$NiCl_2(Pr_3P)_2$]: A; after addition of bromine: B; after addition of nitrosyl chloride: C.

The infrared spectra of the nickel(III) and cobalt(III) phosphine complexes are practically identical with those of the corresponding complexes of the divalent metals, especially the P—C stretching frequency has not been changed significantly (see experimental part).

Dinitrogen trioxide and dinitrogen tetroxide react in a way similar to the nitrosyl halides, *i.e.* in contrast to chlorine and bromine they oxidise not only the nickel(II) phosphine complexes but also the cobalt(II) phosphine complexes to the strongly coloured phosphine complexes of the trivalent metal, reacting as $NONO_2$ and $NONO_3$, respectively, and forming complex nitrites and nitrates with liberation of NO. Our first results [3] seemed to indicate that well-defined compounds could be obtained in this way. For example we once obtained a product with a composition which corresponded quite well to the formula [$NiBr_2(NO_3)(Et_3P)_2$], but this result could not be reproduced. In fact, the nitrogen content of the products varies between 0 and 3 %, but the halogen content varies correspondingly, showing that we have to deal with mixtures of trihalides and dihalidenitrates (or -nitrites). When the products are rigorously purified by extraction with pentane, evaporation of the pentane and again extracting of the residue, the resulting products are the trihalides, containing no nitrogen at all. This result is not surprising because the halogen ions of complex compounds of this type exchange almost immediately on treatment with other anions. Any nitrate or nitrite will therefore be found in the insoluble residue, consisting mainly of nickel(II) and cobalt(II) salts which are always formed as by-products in the preparation of the nickel(III) and cobalt(III) phosphine complexes. The magnetism of several samples of the nitrogen-containing trihalides was measured and they were found to have paramagnetic moments similar to those of the pure trihalides. This also shows that their nitrogen content is due to nitrite or nitrate anions and not to co-ordinated NO. This result has later been confirmed by studying the infra-red spectra of products prepared from [$NiCl_2(Et_3P)_2$] and N_2O_4; the spectra show the absorption band characteristic of the nitrate ion, near 1400 cm^{-1}, but no absorption in the 1600—1800 cm^{-1} region. The yellow nitrites and green nitrates react both with bromine and nitrosyl halides to form dark blue compounds. After addition of bromine or nitrosyl chloride to a benzene solution of $[Ni(NO_2)_2(Pr_3P)_2]$ its absorption spectrum is practically identical with that of a solution of the chloride to which bromine or nitrosyl chloride has been added (*cf.* Fig. 1). However, no trinitrite could be isolated after addition of N_2O_3 to a solution of the dinitrite.

The magnetic moment of the bromide $[NiBr_3(Et_3P)_2]$ was measured in our earlier work[1] as 1.72 Bohr magnetons, corresponding to one unpaired electron. Values near 2 B.M. have been found also for the trichloride, but because of the lability of this compound no exact measurement could be performed. For the more stable cobalt compound $[CoCl_3(Et_3P)_2]$ a paramagnetic moment of 3.0 B.M. has been found, corresponding to two unpaired electrons. Accordingly this compound is not diamagnetic as are most other cobalt(III) complexes, and this would seem to indicate that it actually is a monomolecular 5-coordinated compound and not a bimolecular μ-dichloro compound. However, great care has been taken to determine its molecular weight directly. Some difficulties were encountered because the compound was partly decomposed during measurements of the molecular weight cryoscopically in such solvents as benzene, tetrabromoethane, camphene or cyclopentadecanone. Ebulliometric determinations of the molecular weight of the complex dissolved in ether or dichloromethane by means of the Heitler ebulliometer[5] also gave too small values, indicating dissociation of the compound. However, by means of the indirect (thermoelectric) vapour pressure lowering method, using an apparatus with thermistors[6], the molecular weight of the complex dissolved in chloroform was found to be 409 ± 10, in excellent agreement with the calculated value 401.

Determinations of the dipole moment of this cobalt complex dissolved in benzene gave values between 2 and 3 D, just as we found for the nickel compound $[NiBr_3(Et_3P)_2]$. The cobalt complex is apparently quite stable in benzene solution, but since the nickel complex is decomposed slowly in this solvent[1] we tried to find a more suitable solvent for the measurements of the dipole moments. In pentane both $[CoCl_3(Et_3P)_2]$ and $[NiBr_3(Et_3P)_2]$ were found to have zero dipole moment, *i.e.* the difference between the total polarization and the electronic polarization is only about 30 cm^3. This is the same value as was found for the divalent, square-planar nickel complexes, and it may with great certainty be ascribed to atomic polarization. For the nickel compounds $[NiBr_3(Pr_3P)_2]$ and $[NiBr_3(Bu_3P)_2]$, which we did not obtain quite pure in the solid state, the same result was obtained indirectly by measuring the dielectric constants of solutions of $[NiBr_2(Pr_3P)_2]$ and $[NiBr_2(Bu_3P)_2]$ in pentane after addition of the equivalent amount of bromine.

The results obtained from measurements in benzene solution may be due to dissociation or distortion of the molecules or to formation of a molecular compound with benzene. Since pentane is a more inert solvent than benzene it seems that these compounds in fact have zero dipole moment. This would be in accordance with the trigonal bipyramidal configuration which has also been found for other 5-co-ordinated compounds[7]. It is hoped to get more definite proof of the configuration of the cobalt compound by X-ray determination of its crystal structure.

EXPERIMENTAL

Concerning the microanalyses and the physical measurements see the preceding paper. The KBr-technique could not be used to obtain the infra-red spectra of the Ni(III)- or Co(III)-complexes because they are destroyed during the pressing of the KBr pellets, as shown by a change of the colour and appearance of the strong phosphine oxide band near 1100 cm^{-1} in the spectra. When the nujolmull technique was used this difficulty was avoided. The infra-red spectra of solutions of the complexes in carbon tetrachloride were also recorded, but in these spectra the 700—900 cm^{-1} range is covered by the CCl_4-bands. As in the case of the Ni(II)- and Co(II)-complexes (preceding paper) the infra-red spectra of the Ni(III)- and Co(III)-complexes do not differ essentially from the spectra of the free phosphines.

The molecular weight of $[CoCl_3(Et_3P)_2]$ was determined with a thermistor apparatus[6], built in the laboratory of the Danish Atomic Energy Commission, Risø, Denmark.

Trichlorobis(triethylphosphine)nickel(III), $[NiCl_3(Et_3P)_2]$. A flask containing 200 mg of $[NiCl_2(Et_3P)_2]$ was cooled to -80°C and 1 ml of nitrosyl chloride was distilled into the flask. The temperature was slowly raised until the complex had dissolved in the nitrosyl chloride, forming a dark blue solution, and then the nitrosyl chloride was removed as rapidly as possible by pumping. The residue was dissolved in P_2O_5-dried pentane, the solution was filtered through a glass filter and the solvent removed *in vacuo* as fast as possible without heating. The residue was again dissolved in pentane, filtered and poured into a small glass beaker, which was placed in a vacuum desiccator with P_2O_5 and paraffin. The pentane was slowly evaporated by pumping with an oil pump. In this way well-developed crystals are formed. When most of the pentane had been removed the crystals were filtered off and washed with a little pentane and dried *in vacuo* over P_2O_5 and paraffin. Yield 150—180 mg = 70—80 %, of blue-black crystals soluble in pentane with an indigo-blue colour. M.p. 60—63°C with decomposition (under the microscope the crystals begin to attain a light blue colour at 60°C). (Found: C 34.75; H 7.89; Cl 26.16. Calc. for $C_{12}H_{30}Cl_3NiP_2$: C 35.90; H 7.48; Cl 26.54). In other preparations Cl values ranging from 25.45 to 28.16 % have been found. At room temperature the compound decomposes in less than one day.

The corresponding trimethylphosphine compound is practically insoluble in pentane. It was therefore dissolved in methylene chloride, in which it dissolved with a deep red colour. On evaporating, the compound was obtained as almost black crystals. (Found: Cl 34.70. Calc.: 33.55). The compound can also be prepared directly by adding a solution of chlorine in pentane to a solution of $[NiCl_2(Me_3P)_2]$ in benzene. Yield 85 %. (Found: C 22.80; H 5.98; Cl 30.28. Calc. for $C_6H_{18}Cl_3NiP_2$: C 22.70; H 5.68; Cl 33.55). It has not been possible to prepare this compound quite pure.

Trichlorobis(triethylphosphine)cobalt(III), $[CoCl_3(Et_3P)_2]$. This compound was prepared in the same way as the corresponding nickel compound. The optimum amount of $[CoCl_2(Et_3P)_2]$ to be used for one preparation is about 500 mg, the yield decreasing rapidly with larger amounts. The solution in pentane has a very intense permanganatelike colour and left, on evaporation, violet-black crystals. Yield 80 %. M.p. 102—104°C. (Found: C 35.90; H 7.68; Cl 26.75. Calc. for $C_{12}H_{30}Cl_3CoP_2$: C 35.88; H 7.47; Cl 26.52). Other preparations have given similar values. The compound is considerably more stable than the nickel compound and can be kept in a refrigerator for several months without decomposition.

Molecular weight in chloroform: 409 ± 10 (calc. 401).

Dipole moment in pentane at 25°C ($x = 0.00290$):

P	P_E(calc.)	$P_O + P_A$	P_O	μ(D)
148	118	30	~ 0	0

Magnetic moment:

T	$\chi_g \times 10^6$	$\chi_{mol} \times 10^6$	$\mu_{eff.}$(B.M.)
293	9.68	3880	3.02

Other preparations have given similar values.

The corresponding tripropylphosphine compound was prepared in the same way. It resembles very much the triethylphosphine compound. M.p. 111—113°C. (Found: C 44.25; H 8.61; Cl 21.73. Calc. for $C_{18}H_{42}Cl_3CoP_2$: C 44.50; H 8.65; Cl 21.91).

The corresponding trimethylphosphine compound could not be prepared in this way, because the cobalt(II) complex is decomposed by undiluted nitrosyl chloride. By adding a benzene solution of nitrosyl chloride to a benzene solution of the cobalt(II) complex and evaporating the solvent dark blue crystals, soluble in benzene, methylene chloride, *etc.* with an intensely red colour, are obtained. It has, however, not been possible to obtain the compound in a pure state.

By treatment of the cobalt(II)tributylphosphine complex, which could only be isolated as an oil, with nitrosyl chloride, violet-black crystals, soluble in pentane with red-violet colour, were obtained. The yield is small and the composition is variable. (Found: Cl 18.7; 16.3; 19.6. Calc. for $[CoCl_3(Bu_3P)_2]$: Cl 18.69). The compound decomposes in the course of a few hours.

Tribromobis(trimethylphosphine)nickel(III), $[NiBr_3(Me_3P)_2]$. This compound was obtained — however, not in a quite pure state — by adding a solution of bromine in pentane to a solution of the nickel(II) complex in benzene. It was precipitated as almost black crystals, soluble in methylene chloride or benzene with an intense red colour, but insoluble in pentane. As mentioned in the foregoing paper it is formed already on exposure of an ethanolic solution of the nickel(II) compound to air. (Found: C 15.60; H 4.18; Br 51.60. Calc. for $C_6H_{18}Br_3NiP_2$: C 15.98; H 4.00; Br 53.23).

Tribromobis(triethylphosphine)nickel(III), $[NiBr_3(Et_3P)_2]$. This compound, which we had prepared earlier [1] by reaction of $[NiBr_2(Et_3P)_2]$ with bromine, could also be prepared by adding a benzene solution of nitrosyl bromide to a benzene solution of the nickel(II)-complex. It is not possible to use the same method as was used to prepare the chlorides because nitrosyl bromide can not be distilled without decomposition. The use of a solvent has the disadvantage that it takes some time to remove the solvent, during which some decomposition of the complexes takes place.

After removal of the solvent *in vacuo* and extraction of the residue with pentane as described for the chloride the compound was obtained as almost black crystals, soluble in pentane with an intense green colour. Yield about 80 %. M.p. 83—84°C (or a few degrees lower when determined under the microscope). (Found: Br 45.18. Calc.: Br 44.86).

Dark green tripropylphosphine and tributylphosphine compounds were obtained similarly, but not in a quite pure state. The dipole moments of these two compounds were determined by measuring the dielectric constant of solutions of the corresponding nickel(II)-complexes in pentane after addition of the equivalent amount of bromine.

All three compounds were found to have dipole moment zero:

	P	P_E (calc.)	$P_A + P_O$	P_O	μ
$[NiBr_3(Et_3P)_2]$	157	126	31	~ 0	0
$[NiBr_3(Pr_3P)_2]$	186	154	32	~ 0	0
$[NiBr_3(Bu_3P)_2]$	217	181	36	~ 0	0

Tribromobis(triethylphosphine)cobalt(III), $[CoBr_3(Et_3P)_2]$. This compound was prepared in the same way as the corresponding nickel compound. On addition of nitrosyl bromide to a benzene solution of the blue cobalt(II)-complex an intensely green coloured solution is obtained. The solution in pentane is green in reflected, but red in transparent light. This bromide is less stable than the corresponding chloride and was only obtained in slight yield and not quite pure. M.p. 87—89°C. (Found: C 26.50; H 5.93; Br 44.00. Calc. for $C_{12}H_{30}Br_3CoP_2$: C 26.94; H 5.61; Br 44.86).

The corresponding trimethylphosphine compound was obtained in a similar way, but not in a pure state. It is soluble in benzene and methylene chloride with an intense red colour, but almost insoluble in pentane.

From the nickel(II) compounds of tricyclohexylphosphine and tribenzylphosphine and nitrosyl bromide dark green compounds were obtained. Bromine analyses indicated, however, that bromination of the ligand had taken place and the products were not investigated further.

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