[CONTRIBUTION FROM THE INSTITUTE OF GENERAL CHEMISTRY, THE UNIVERSITY OF PALERMO, PALERMO, ITALY]

Metal Complex Formation in Non-hydroxylic Solvents. III. The Thermodynamics of Interaction between Trialkyl-amines and -phosphines and NiDBH in Benzene[1,2]

BY L. SACCONI, G. LOMBARDO AND P. PAOLETTI

RECEIVED DECEMBER 28, 1959

The formation constants, heats of reaction and free energy and entropy changes associated with the equilibria between diacetyl-bisbenzoylhydrazino-nickel(II) and trialkyl-amines and -phosphines in benzene have been determined spectrophotometrically. The donor tendency of trialkylamines is governed by a competition between steric and inductive effects. While the stability of the adducts of phosphines is 4–11 times that of amines, the heats of formation are practically equal for both series of ligands. These data are discussed in terms of steric and electronic factors. The higher stability of the phosphine adducts is ascribed to the presence of lower steric strains. The bonding between nickel and phosphine ligands appears to be essentially σ in character. Triphenyl-amine, -phosphine, -arsine and -stibine do not coördinate to NiDBH probably owing to resonance and steric effects.

Several characteristics of metal complexes have been explained by the hypothesis of dative π-bonding. Among these are the reduced metal–ligand bond distance,[3] the *trans*-effect,[4] the ligand field splitting calculated from the ultraviolet spectra,[5] the stability constants,[6] the shift in the infrared frequencies,[7] etc.

The nature of this type of bond has not, however, been sufficiently elucidated.

The donor atom that has been mainly considered as capable of forming π-bonds is phosphorus, and many stable metal complexes with trivalent phosphorus ligands have been described and studied. The possibility of forming double bonds, however, depends also upon the nature of the metal atom. For instance, while the π-character of bonding between phosphines and platinum(II) seems well established on the basis of *trans*-effect,[4] the importance of a π-component in the nickel-phosphine bond is still under discussion.[7,8]

The knowledge of the bond strength of the nickel–phosphine bonding could throw some light on this problem. Unfortunately there are no thermodynamic data on the bond strength between phosphorus and transition metal atoms, determined from the enthalpy of formation of the complexes. This results from nearly all the formation equilibria of complexes having been studied in aqueous or hydroxylic media in which the trivalent phosphorus ligands, such as phosphines, generally undergo decomposition.[9] Furthermore no entropy data, which are so indicative of the steric factors influencing the metal-ligand interaction, do exist for such equilibria.

Therefore it was thought advisable to use the planar complex NiDBH[10] as a reference acceptor for trialkylphosphines in order to determine the thermodynamic functions ΔF, ΔH and ΔS for the formation of the $NiDBH \cdot 2PR_3$ adducts in benzene. In addition the formation equilibria of the $NiDBH \cdot 2NR_3$ adducts have been studied. In this way it was possible to compare the coördinating affinities of the two series of analogous ligands and the strength of the Ni–N and Ni–P bonds under similar conditions and in the absence of polar solvents. The data so obtained have been used mainly to discuss the nature of the nickel–phosphine bondings.

Experimental

Materials.—The trialkylamines, which were good-quality commercial products, were purified by standard methods until their physical constants agreed closely with the values in the literature. They were dried on potassium hydroxide and distilled in a Todd fractionating column and the constant boiling middle fractions collected. Trimethylamine was used without purification. The trialkylphosphines were prepared according to the data in the literature[11] and were purified by distillation under reduced pressure avoiding contact with atmospheric humidity. The concentrations of nitrogen bases in the benzene solutions were determined by titration as previously reported.[12]

Spectrophotometry and Calculation of Thermodynamic Quantities.—The spectrophotometric measurements were made and the thermodynamic data were calculated as described in the previous paper.[12] The absorption curves for trialkyl-amine and -phosphine adducts in the range investigated are quite similar to those of pyridines already reported.[10] They have a sharp isosbestic point lying between 410 and 430 mμ and an absorption maximum in the 460–480 mμ region.

The accuracy of the values of the thermodynamic functions is ΔF, ± 0.05; ΔH, ± 0.3 kcal./mole; ΔS, ± 0.7 e.u.

Results and Discussion

The thermodynamic data are given in Tables I and II. The negative values of the Taft constants $\Sigma\sigma^*$ also are reported.

The series of donor tendencies of the amines, evaluated on the basis of the inductive substituent constant σ^*, is $NMe_3 < NEt_3 < NPr_3 < NBu_3$,[13]

---

[1] This research was supported by the U. S. Department of the Army through its European Research Office, under Contract No. DA-91-508-EUC-304.

[2] Presented at the International Conference on Coördination Chemistry, London, April, 1959.

[3] L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 250.

[4] J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955), and references quoted therein.

[5] J. Chatt, G. A. Gamlen and L. E. Orgel, *ibid.*, 1049 (1955).

[6] R. K. Murmann and F. Basolo, THIS JOURNAL, **77**, 3484 (1955).

[7] L. S. Meriwether and M. L. Fiene, *ibid.*, **81**, 4200 (1959).

[8] (a) R. S. Nyholm, *Chem. Revs.*, **53**, 263 (1953); (b) R. S. Nyholm and L. N. Short, *J. Chem. Soc.*, 2670 (1953); (c) L. A. Woodward and J. R. Hall, *Nature*, **181**, 831 (1958); (d) J. Chatt and F. A. Hart, *Chem. & Ind. (London)*, 1474 (1958); (e) W. S. Fyfe, *J. Chem. Phys.*, **28**, 907 (1958).

[9] *Cf.* H. M. N. H. Irving, "The Stability of Metal Complexes," in "Lectures Delivered and Abstracts of Paper Submitted," International Conference on Coördination Chemistry, London, April 1959, Special Publication No. 13, The Chemical Society, London, 1959; S. Ahrland, J. Chatt and N. R. Davies, *Quart. Revs. (London)*, **12**, 265 (1958).

[10] L. Sacconi, G. Lombardo and P. Paoletti, *J. Chem. Soc.*, 848 (1958).

[11] H. Hibbert, *Ber.*, **39**, 160 (1906); W. C. Davies and W. J. Jones, *J. Chem. Soc.*, 33 (1929); W. C. Davies, P. L. Pearse and W. J. Jones, *ibid.*, 1262 (1929).

[12] L. Sacconi, G. Lombardo and R. Ciofalo, THIS JOURNAL, **82**, 4181 (1960).

[13] H. K. Hall, Jr., *ibid.*, **79**, 5441 (1957).

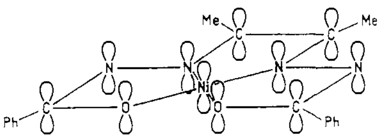

Fig. 1.—The π-bond system of the coördinated conjugate rings of NiDBH. Only the d_z2 among the d-orbital of nickel atom is represented.

that is, the polarity increases in going through the series. With the proton as acceptor, which has a very low F-strain factor, the series of donor capacities is, $NMe_3 < NEt_3 > NPr_3 > NBu_3$. This behavior has been ascribed by Brown[14] to a competition between the polar effect of alkyl chains and steric strain (essentially B-strain).

Table I

Formation Constants of NiDBH Adducts with Normal Trialkyl-Amines and -Phosphines in Benzene Solutions

Base	log $K_{10°}$	log $K_{25°}$	log $K_{45°}$	pK_a[a]
NMe_3	3.88 ± 0.04	3.40 ± 0.04	2.70 ± 0.05	9.80
NEt_3	1.84 ± .02	1.32 ± .03	0.71 ± .03	10.74
NPr_3	1.38 ± .02	0.88 ± .02	.26 ± .02	10.65
NBu_3	1.01 ± .03	0.51 ± .04	.11 ± .04	9.33
PEt_3	6.72 ± .05	6.18 ± .04	5.54 ± .05	
PPr_3	6.25 ± .05	5.74 ± .04	5.08 ± .04	
PBu_3	6.30 ± .05	5.76 ± .05	5.11 ± .05	

[a] N. F. Hall and M. R. Sprinkle, This Journal, **54**, 3469 (1932).

Table II

Thermodynamic Functions for the Equilibria NiDBH + 2 Base ⇄ NiBDH·2 Base at 25° in Benzene Solutions

Base	$-\Delta F$ (kcal./mole)	$-\Delta H$ (kcal./mole)	$-\Delta S$ (e.u.)	$-\Sigma\sigma^*$
NMe_3	4.63	13.9	31.0	0.00
NEt_3	1.86	13.3	38.2	+ .03
NPr_3	1.20	13.2	40.3	+ .35
NBu_3	0.69	13.1	41.8	+ .39
PEt_3	8.43	13.9	18.3	
PPr_3	7.85	13.8	19.9	
PBu_3	7.85	14.8	20.6	

We have found that the donor affinity toward NiDBH decreases steadily from NMe_3 upwards according to the series: $NMe_3 > NEt_3 > NPr_3 > NBu_3$. This would indicate that the steric factors opposing the inductive effect are more important in this case than when the reference acid is the proton. In fact, while with the hydrogen ion the steric strain begins to prevail over the inductive effect at NPr_3, in the case of NiDBH the steric effect is predominant in every case. On account of the flat and extended structure of NiDBH there should be, in addition to B-strain, a F-strain which increases as the alkyl chains become more bulky and protrude beyond the nitrogen toward the atoms of the NiDBH plane.

The strength of the Ni–N bonds in the trialkylamine adducts evaluated from ΔH values is practically constant within experimental error. The entropy changes are negative, as a result of the decrease in the number of particles present due to the formation of six-coördinated complexes and the over-all increase in the rigidity of the system. The $-\Delta S$ values increase steadily from NMe_3 to NBu_3 showing that the reduction in the freedom of rotation of the amines around the Ni–N bonds, mainly due to F-strain, increases as the alkyl chains lengthen. These data show that the stability of the complexes is essentially an entropy effect.

Similar increases in the negative entropy changes were found for the NiDBH adducts with *o*-substituted methyl-pyridines and were likewise ascribed to steric effect (*o*-effect).[10]

In the case of phosphines the free energy changes are 4.5 to 11 times higher than those of the corresponding trialkylamines. On the other hand, the heat of formation is constant within experimental error for the different phosphines, being practically equal to that of trialkylamines.

The fact that the bond strength is equal for amines and phosphines may be taken as an indication that the π-character of the nickel-phosphine bond in the NiDBH adducts is negligible. This can be attributed: (i) to the fact that trialkylphosphines do not readily function as π-bond acceptors; (ii) to a low π-bond donor ability of the Ni in NiDBH.

The first hypothesis is in accordance with the conclusion of many recent studies. The measurements of the strength of *trans*-effect in planar Pt(II) complexes,[15] for instance, indicate that the π-bonding ability of trialkylphosphines is the lowest among the other trivalent phosphorus ligands. Also the X-ray Ni–P distance in the $NiBr_2{\cdot}2PEt_3$ complex has been found to be that of a single bond.[16]

The second hypothesis, however, also may be taken into consideration. In fact, the nickel of NiDBH is the center of a π-bond system of the three conjugate chelate rings (Fig. 1). The d_{xz} and d_{yz} orbitals of nickel may overlap with the p_z orbitals of the four ligand atoms, being thus available for π-bonding with phosphines for only a small part of the time. It may be remembered, however, that the entropy data for the equilibria between pyridine bases and NiDBH allowed the contribution of some double bond character to the Ni–N bonding in the pyridine adducts.[10]

Also the ΔS values for phosphines indicate the predominant σ-character of the Ni–P bonds. In fact the negative entropy changes found for phosphines are about one half of those found for trialkylamines. This suggests that, in the NiDBH adducts, the phosphines are less constrained than the amines. If Ni–P bond had a large double bond component, on the contrary, this should result in more negative entropy change with respect to the corresponding amines as a consequence of a hindered rotation around the Ni–P double bond. Such a decrease was found on passing from piperidine to pyridine adducts of NiDBH and it was interpreted in terms of π-bond formation.[10] It should be remembered, at least, that the double bonding character was found to be quite moderate for the bonds between phosphine and zerovalent nickel[7,8c,d]: there is even greater reason to assume this for the bonds with bivalent nickel because in

---

(14) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(15) J. Chatt and A. A. Williams, *ibid.*, 3061 (1951); E. A. Magnusson, *Revs. Pure and Appl. Chem.* (*Australia*), **7**, 195 (1957).

(16) V. Scatturin and A. Turco, *J. Inorg. & Nuclear Chem.*, **8**, 447 (1958).

this case the d electrons of the metal will be held more strongly and so will be less available for dative π-bonding.

The fact that in the NiDBH complexes the phosphines appear to be less constrained than the amines can be attributed to a decrease in F- and B-strain. In fact, the atomic radius of phosphorus (1.10 Å.) is about 0.40 Å. larger than that of nitrogen (0.70 Å.). As a consequence, with the phosphine adducts, the alkyl chains will be 0.8 Å. further away from the NiDBH plane than with the amine adducts. It is therefore expected that the F-strain will be much weaker, or lacking, in phosphine complexes. Moreover, B-strain is to be considered as absent in trialkylphosphines[17] because of the larger size of P as compared with N, and because the C–P–C angles (100° in trimethylphosphine) are less than tetrahedral and are smaller than the C–N–C angles in trialkylamines (108–109° for trimethylamine).[18] In this case, as suggested by Spitzer and Pitzer, B-strain may be more base-strengthening than base-weakening.[19]

In conclusion the higher stability of phosphine adducts in comparison with that of amines appears ascribable to the lower steric strain between phosphines and NiDBH.

Equilibria between Triphenyl-amine, -Phosphine, -Arsine and -Stibine and NiDBH.—The coördinating ability of these substances toward transition metal atoms is well established. Many stable metal complexes of triphenyl-amine, -phosphine, etc., have been described.[20] These ligands, however, show no coördinating tendency toward NiDBH: solutions of the complex do not turn brown on addition of these bases. This fact can be accounted for in terms of steric and electronic effects.

As is well known, the phenyl group, on account of the resonance effect, is an electron-withdrawing substituent and so decreases the σ-bonding tendency of the ligands and increases their π-bonding ability. Since the nickel–phosphorus bonding in the NiDBH adducts appears to be essentially σ in character, the Ni–P bonding will be much too weak and so the adducts with triphenylphosphine will not form. This reason holds also for triphenylarsine, etc. For triphenylamine one can also invoke the influence of steric factors. In fact, in this triphenyl derivative the three phenyl groups lie preferably in planes at 120° passing through the axis of the pyramid having the nitrogen as vertex. For this reason the phenyl groups will protrude beyond the N atom. This does not give rise to steric hindrance when the triphenylamine is bound to a tetracoördinated metal atom at one of the four vertices of the square or tetrahedron. However, in the case of NiDBH, it is to be expected that the phenyl groups which coördinate to the nickel atom above and below the equatorial plane of NiDBH will interfere with the atoms in such plane. On the other hand, the three phenyl groups cannot avoid this strain by rotation without clashing.

---

[17] H. C. Brown, THIS JOURNAL, **67**, 503 (1945); H. C. Brown, D. H. McDaniel and O. Häfliger, in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., Publ., New York, N. Y., 1955, p. 642.

[18] L. O. Brockway and H. O. Jenkins, THIS JOURNAL, **58**, 2036 (1936); H. D. Springall and L. O. Brockway, *ibid.*, **60**, 996 (1938).

[19] R. Spitzer and K. S. Pitzer, *ibid.*, **70**, 1261 (1948).

[20] W. Reppe and W. J. Schweckendieck, *Ann.*, **560**, 104 (1948), K. Yamamoto, *Bull. Chem. Soc. Japan*, **27**, 501 (1954); L. M. Venanzi, *J. Chem. Soc.*, 719 (1958); L. Vallarino, *J. Inorg. & Nuclear Chem.*, **8**, 288 (1958); J. Chatt and G. A. Rowe, International Conference on Coördination Chemistry, London, April, 1959, Abstract No. 8.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

Ruthenium(III) Chloride Complexes: $RuCl_2^+$

BY ROBERT E. CONNICK AND DWIGHT A. FINE

RECEIVED JANUARY 8, 1960

Ruthenium in the + 3 oxidation state in aqueous solution is known to form a number of complexes with chloride ion which equilibrate only slowly. Because of the complexity of this system, only one of these, $RuCl^{+2}$, previously has been isolated in solution and identified unambiguously. In the present study two more of the complexes have been obtained in pure form and characterized. The formulas of these complexes, which are cationic species, have been determined by use of properties of ion-exchange resins. The total charge per species was determined by equilibrating the unknown species and hydrogen ion with ion-exchange resin in a pair of experiments. The charge per metal atom on one species was determined by a modification of a previously reported method involving the pushing of the species from an ion-exchange column with an ion of known charge. The salt of a weak acid had to be used to produce a concentrated band. The charge per metal atom of the other species was established by determination of the amount of a known ion displaced from an ion-exchange column by a solution of the species. The number of chloride ions bound to the metal atom was determined by direct analysis. The species were both found to have the formula $RuCl_2^+$ and are presumed to be *cis* and *trans* isomers. The species were separable by elution from an ion-exchange column.

Introduction

In a previous paper, a method for the determination of the formulas of aqueous ruthenium(III) species which equilibrate only slowly was described.[1] This method involves the use of ion-exchange resins to determine the charge per metal atom and the charge per species. The formula may be inferred from these two data if only one type of complexing anion is involved. The method was used to identify the species Ru^{+3} and $RuCl^{+2}$. A third species was identified tentatively as $RuCl_2^+$. A more definite identification of the latter species was desired, as well as the identification of other ruthenium(III) species present in hydrochloric acid solution.

---

[1] H. H. Cady and R. E. Connick, THIS JOURNAL, **80**, 2646 (1958).