A π-Bonded Azobenzene Complex. The Structure of Bis(*tert*-butyl isocyanide)(azobenzene)nickel(0)

Sir:

It was first suggested[1] in 1936 that the N=N function in azo compounds should be capable of forming olefin-like π bonds to transition metals. However, previous studies on 1:1 transition metal–azo compounds have revealed only structures in which the nitrogen lone pair acts as the σ-donor site.[2] The structure of a cuprous chloride–azomethane complex is of similar type.[3] In two structures where an azo function bridges two iron atoms,[4,5] the bonding is thought to be more consistent with a metal-to-nitrogen σ interaction than with the π-bonded model. Within the last year, Otsuka and coworkers[6] and simultaneously Klein and Nixon[7] have reported the formation of azobenzene–nickel(0) complexes which, on the basis of displacement reactions and spectroscopic properties, appear to incorporate the azobenzene as a side-bonded, olefin-type ligand.

The importance of π organotransition metal complexes in homogeneous catalysis, coupled with the probability that coordination of the simple azo compound diimide (HN=NH) plays a significant role in the nitrogen-fixation process, has prompted us to investigate the solid-state structure of one of these compounds.

We have determined the structure of bis(*tert*-butyl isocyanide)(azobenzene)nickel(0), $Ni(C_6H_5N{=}NC_6H_5)((CH_3)_3CN{\equiv}C)_2$, from three-dimensional X-ray data collected by counter methods. The compound crystallizes from diethyl ether as red, needle-like plates in the monoclinic space group $C_{2h}{}^5$-$P2_1/c$. The unit cell contains four molecules and has dimensions a = 12.404 (8), b = 17.154 (8), c = 12.487 (6) Å, β = 117.46 (6)°. A total of 2694 absorption-corrected structure amplitudes with $F_o{}^2 > 3\sigma(F_o{}^2)$ were used in the solution of the structure. This solution was obtained by a combination of Patterson and difference Fourier methods. A mixed isotropic–anisotropic least-squares refinement has led to a current value of R of 0.070 (where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$).

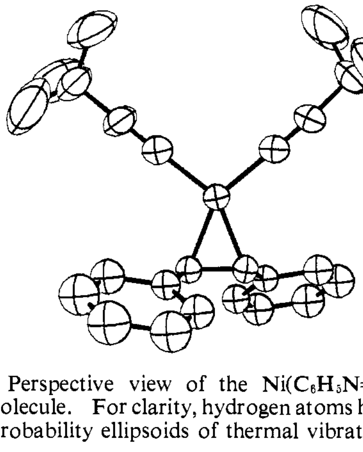

Figure 1. Perspective view of the $Ni(C_6H_5N{=}NC_6H_5)((CH_3)_3CN{\equiv}C)_2$ molecule. For clarity, hydrogen atoms have been omitted. The 50% probability ellipsoids of thermal vibration are shown.

Figure 1 presents a drawing of the molecule. If the azobenzene is regarded as a single ligand, the coordination about the nickel atom is trigonal. The dihedral angle between the Ni-NN (of azobenzene) and the Ni-CC (of *tert*-BuNC) planes is only 1.2 (3)°, while the N-N vector makes an angle of 88.8 (3)° with the normal to the Ni-CC plane. Hence, the inner coordination sphere of the molecule is essentially planar. This feature of the structure contrasts with the observation[8] of a considerable dihedral angle (about 24°) between the Ni-CC (of TCNE) and Ni-CC (of *tert*-BuNC) planes in the related complex bis(*tert*-butyl isocyanide)(tetracyanoethylene)nickel(0). The average distance from the nickel to the α-carbon atoms of the *tert*-BuNC groups is 1.840 (5) Å; this is somewhat shorter than the corresponding distance of 1.866 (5) Å in the related $Ni(TCNE)((CH_3)_3CN{\equiv}C)_2$ complex[8] and may indirectly reflect the weaker electron-withdrawing effect of azobenzene relative to tetracyanoethylene. The C≡NC fragment of the azobenzene complex is very nearly linear, with average C≡N and N—C distances of 1.154 (6) and 1.441 (6) Å, respectively. The $C{-}CH_3$ distances average 1.44 (1) Å. The nitrogen atoms of the azobenzene ligand are equidistant from the metal, with a Ni-N distance of 1.897 (4) Å. The N-N distance of 1.385 (5) Å for the coordinated azobenzene is significantly longer than the corresponding distance in the free ligand, where distances of 1.23 and 1.17 Å have been reported[9] for the two different molecules in the asymmetric unit of *trans*-azobenzene. Indeed, the observed N-N distance is very close to the N-N single bond length[4] of about 1.40 Å. In free *trans*-azobenzene, neither of the two independent molecules is planar; rather, the phenyl rings are twisted 17 and 6° from ideal planarity.[9] The corresponding twist of the phenyl rings in the present coordinated azobenzene is approximately 14°. In addition, there is a further distortion of a type commonly found with coordinated olefins.[10] Thus, there is a dihedral angle of 26.8° between the two N-N-C(phenyl) planes. This angle would be 0° if the C-N-N-C′ portion of the molecule were planar as it is in free *trans*-azobenzene.

Both the bond lengthening and the geometry within the coordinated azobenzene are consistent with the usual descrpition[11,12] of the π bonding of olefins to transition metals. On the basis of this bonding model, we would predict forward donation from the π orbitals of azobenzene to vacant metal orbitals and a concomitant back donation from filled metal orbitals to π^* antibonding orbitals of the N=N interaction. There is no indication that the nitrogen lone pairs affect the azobenzene-to-metal bonding in any way.

The biological fixation of nitrogen and its reduction to ammonia are believed to involve transition metal species. It has been suggested[13] that the process involves two metal sites, one to hold hydrogen and the other to bind nitrogen loosely. Reaction of the metal

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(1) M. S. Kharasch and T. A. Ashford, *J. Amer. Chem. Soc.*, **58**, 1733 (1936).

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(6) S. Otsuka, T. Yoshida, and Y. Tatsuno, *Chem. Commun.*, 67 (1971).

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(12) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951).

(13) G. W. Parshall, *J. Amer. Chem. Soc.*, **89**, 1822 (1967), see references to R. W. F. Hardy and E. Knight.

hydride with the transient N_2 complex could then give an adduct (such as a diimide complex) which could subsequently be reduced stepwise to ammonia. The recent studies of Armor and Taube on the π-bonded state of N_2–transition metal complexes[14] and our confirmation of the π-bonded structure for this RN=NR complex provide models for consideration of the possible role of π-bonded diimide in the biological nitrogen fixation process.

(14) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **92**, 2560 (1970).

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*Book Reviews**

Chemical Kinetics. Second Edition. By B. Stevens. Chapman and Hall, Ltd., London. 1970. viii + 110 pp. $2.00.

Note from the publishers: The review of this title in the April 7th, 1971 issue of this Journal contained reference to a printing error which the reviewer surmised was present in all copies. We would like to take this opportunity of stating that this is not the case, that, in fact, the error will be found in exceptionally few copies, and that we will undertake to replace those offending copies returned to us.

In view of the above assurance from the publishers, the reviewer can now recommend this book as a conveniently concise exposition of the essentials of kinetics, suitable for students reviewing the subject.

Chimie. Volume I. Mesures, Constantes physiques des corps chimiques. 69th Edition. By J. Jousset. Dunod, Paris. 1971. xxix + 248 + XL pp. 9.6 francs.

This European minihandbook fits into a hip pocket and carries a remarkable amount of information in its twelve chapters: Measures; The Atom; Thermal Data; Optical Data; Densities, Vapor Pressure and Azeotropes; Solubilities; Solvents; Viscosities; Surface Tensions; Toxicology; Physico-chemical Relationships. Since it is composed almost entirely of tables, language need be no barrier, and the headings are obvious in meaning. An example of the useful tables is one listing organic compounds in formula-index order, and giving for each the molecular weight, state, specific heat, heat of formation, melting point, boiling point, heat of vaporization, heat of combustion, expansion coefficient, and thermal conductivity. There is also a useful pair of tables giving melting points and boiling points in numerical order by five-degree intervals in astonishingly compact form. At $2.50, one can't go wrong!

The Condensed Chemical Dictionary. Eighth Edition. Edited by G. G. Hawley. Van Nostrand-Reinhold Co., New York, N. Y. 1971. xiii + 971 pp. $27.50.

With this edition, this useful reference work has passed its fiftieth birthday. The entries vary in size from one line to the larger part of a column, and average twenty to a page. The types of subjects included cover a broad range of technical descriptions and uses, definitions, and identification of a very large number of trade names and abbreviations. A few examples taken from the letter "R" will illustrate the scope: Reaumur (a temperature scale); refinery gas; relaxin (a hormone obtained from pregnant sows); Reppe process; resonance; RFNA (biochemicalese for red fuming nitric acid); Rossville Alcohol (ethanol); Rubinol (an alizarin dye); Rust (a form of dusting sulfur); Rutherford, Sir Ernest. The definitions and descriptions are generally excellent, being concise and accurate, although inevitably there are a few that fall short, such as the entry for nitrilotriacetic acid, which does not suggest its large-scale use in the detergent field. The Dictionary is fascinating to browse through as well as being a reference source.

Industrial and Specialty Papers. Volumes I to IV. Edited by R. H. Mosher (R. M. Associates) and D. S. Davis (University of Alabama). Chemical Publishing Co. Inc., New York, N. Y. 1970. xii + 328 pp., x + 330 pp.; vi + 375 pp., and iv + 240 pp. $12.00 per volume.

These volumes are subtitled "Technology," "Manufacture," "Applications," and "Product Development." Each is composed of contributed chapters of widely varying authorship, of largely industrial origin. In our prepackaged, gift-wrapped world, specialty papers have become an essential to existence, and range from disposable diapers through alteration-proof bank checks to cigarette filters, and it is appropriate for chemists to become familiar with the foundations of the subject. The chemistry covered in this work is not generally very sophisticated, but the applications are often ingeniously so. There are chapters on such subjects as "Theory of High Polymers and Their Application to the Paper-Converting Industry" and "Laminating and the Theory of Adhesion," as well as sections on the engineering and marketing aspects of the subject. There is much of interest to the general reader, and the set could be invaluable to the chemist contemplating employment in a new field. Substantial bibliographies, and separate indices for each volume, support the reference value of the work.

Photochemistry. By R. P. Wayne (Oxford University). American Elsevier Publishing Co., Inc., New York, N. Y. 1971. iii + 263 pp. $12.00.

For many years the field of photochemistry had been poorly represented in terms of published textbooks. Fortunately, this condition has been alleviated recently by the publication of fine compendia at the research level. For the undergraduates and nonspecialist research students, however, there still existed no suitable introductory text in photochemistry.

To meet this need R. P. Wayne has produced an admirable text, providing a good survey of the basic areas of photochemistry but also including the excitement of detailed involvement. A well-written book, "Photochemistry" brings together the various areas of physical chemistry such as spectroscopy, energy transfer, and kinetics.

Chapters 1 and 2, Basic Principles of Photochemistry and Absorption and Emission of Radiation, in themselves afford students a good, yet uncomplicated foundation. Photodissociation, which is covered in Chapter 3, is a fine introduction to this important process and includes many illustrative examples. In Chapters 4 and 5 the author explores the complexities of the emission process. The author then expands his coverage in the next two chapters on Reaction of Excited States and Techniques in Photochemistry. In the final chapter, Photochemistry of Action, a host of applied examples, *e.g.*, atmospheric photochemistry, polluted atmospheres, photosynthesis, vision, photochromism, optical brighteners, etc., makes one marvel at the details of the photochemical process. For the inspired student the carefully chosen bibliography is an excellent guide for further study.

H.-G. Gilde, *Marietta College*

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