Coordination Chemistry Reviews, 26 (1978) 1–5

THE RESEARCH RECORD OF A.D. ALLEN — AN APPRECIATION *

The discovery by Allen and Senoff [17] of the first dinitrogen coordination compound represented such a break with tradition and is of such importance that it has tended to overshadow, and thus obscure, Allen's other contributions to chemistry. Though fortune undoubtedly played a role in this, as it does in most discoveries, a study of the record of Allen's earlier work makes it clear that there was also an important component of the inevitable in it.

Allen's tastes in chemistry were eclectic. His earliest researches were in the field of physical organic chemistry and dealt with the mechanism of substitution on N(III) [1,2,6,7]. His research began to touch on the inorganic realm when he turned to the study of the mechanism of substitution at silicon in organosilicon compounds [3,4,5], a particular interest that continued quite late into his scientific career [26]. He then turned to orthodox organometallic systems [8–14], where he focussed on phosphine and acetylene complexes of platinum(0) and platinum(II). The progression of interest then continued [15] to classical coordination complexes, and it was in the course of pursuing this particular line of work that the species $Ru(NH_3)_5N_2^{2+}$ was discovered.

Matching the breadth of his interest in the descriptive matter, was his versatility in bringing a variety of approaches to bear on the study of the systems he had selected, and his mastery of a wide range of chemical principles. Often, interest and competence in preparative coordination chemistry is accompanied by an interest in structure, but seldom does it include, in addition, the systematic study of reactions. Conversely, many who are engaged in the systematic study of reactions depend on others for structural information, and are creative in preparations only to the extent demanded by their central concern. There is no evidence of this kind of limitation of scope in Allen's work, and he used whatever approach was necessary to do a thorough job of understanding the system at hand.

His early work involved application of the various strategies that are appropriate to defining the mechanism of substitution — determination of reaction kinetics, application of stereochemical principles, of solvent effects, and isotopic tracer techniques. An interest in the consequences of back bonding, and its effect on stabilities and labilities, seems to have motivated his entry into the field of organometallic chemistry. The paper with Cook given at a symposium on organometallic compounds [12] summarizes his ideas on, and attitudes to, this subject area. Equilibrium constants governing the replacement of one

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* References to the Allen bibliography will be given without a letter prefix; those to the general literature will be preceded by R.

ligand by another, and the rates governing the reactions were important to him, as were the structural effects, geometrical and electronic, that gave rise to the differences. These observations were rationalized in terms of inductive effects, which influence the σ and π (back-bonding) components of the binding. He clearly recognized the importance of steric requirements, not as minor perturbations but as having the power to affect even compositions in a drastic way. Thus he and Cook [8] proved that a compound containing three molecules of $(p\text{-}FC_6H_4)_3P$ per Pt, which had been claimed by others to contain also hydride, was in fact the tris-phosphine complex of Pt(0). Furthermore, in discussing the kinetics of replacement from $(Ph_3P)_2Pt(p\text{-}C_6H_4CCH)$ of the bound acetylene by another, Allen and Cook [11] make the comment "...examination of the kinetics...indicates that the intermediate formed in the rate determining step, $(Ar_3P)_2Pt$, has a significant stability..." The record of his work with organometallic complexes is brief, but it suffices to show that Allen was early in introducing systematic studies of reaction dynamics and that he had a great deal of insight into the chemistry of organometallic complexes. It is apparent that if he had been able to continue he would have done a great deal to advance the systematization of this important, rich and complex field.

The stage had by now been prepared for the discovery of $(NH_3)_5RuN_2^{2+}$. It is a reasonable conjecture that he turned to the rutheniumammines because of a desire to extend to some classical coordination complexes his concern with basic aspects of the mechanisms of substitution. While up to that time a great deal of work had been done on substitution in cobaltammines and in complexes of platinum(II), other substitution-inert centers had received little attention and it was important to learn in what way conclusions based on studies already done could be generalized. It is also a reasonable conjecture that in modifying a published procedure by replacing hydrazine monochloride in the preparation of $Ru(NH_3)_5Cl^{2+}$ from ruthenium trichloride [R1,R2] by hydrazine hydrate, he was relying on his previous experience in which the latter compound had been used to reduce Pt(II) to Pt(0) [8]..

Whatever the detailed history of the preparation of the first dinitrogen complex, the important point is that Allen and Senoff did not discard the substance simply because it was not the product expected and desired. If pure scientific curiosity had not been highly developed in Allen, and if he had not been expert in the variety of skills needed to learn what in fact had been prepared, it would have been easy to set the awkward material aside and to repeat the preparation of $[Ru(NH_3)_5Cl]^{2+}$, now following in detail the procedure described in the literature.

When the report by Allen and Senoff appeared, there were undoubtedly a few who were not astonished that a metal complex of dinitrogen could exist. Fewer in number were those who were prepared for the observed kinetic stability of $[Ru(NH_3)_5N_2]Cl_2$, and still rarer were those who were prepared for what soon became established fact, that the dinitrogen complexes could be produced by the direct reaction of elementary nitrogen [R3,R4] even with rather stable reagents under quite ordinary conditions [R5]. The first flush of optimism that this new chemistry would lead to improved methods for converting dinitrogen to commercially useful products was soon dissipated, but the interest in this possibility, bolstered also by Vol'pin's [R6] discoveries, has been permanently established by the new chemistry that was motivated by, and based upon, the Allen and Senoff contributions. The reduction of dinitrogen in *d*-electron rich species has been demonstrated [R7,R8], and other mechanisms for the reduction will undoubtedly be discovered. Even more remarkably, the direct incorporation of carbon residues into the reduction product of N_2 ligated to *d*-electron rich metals has been achieved [R9], as had already been realized by using titanium in a low oxidation state as a reducing agent [R10,R11]. From this kind of chemistry at least, one can be confident that important industrial processes will in due time emerge.

While the possible relevance of the Allen and Senoff discovery to the commercial and biological utilization of dinitrogen has attracted the widest attention, it may well be that its greatest importance will prove to lie in the inorganic chemistry of this ligand, the dinitrogen complexes acting, for example, as intermediates in providing new preparative approaches, and possibly some compounds having unique and useful properties in their own right. Allen and co-workers [27,28] themselves exploited some of the preparative opportunities which the Allen and Senoff ion opens up in ruthenium chemistry. Quite remarkable is the fact that the original recipe for the production of the species $Ru(NH_3)_5N_2^{2+}$ serves also for the formation of the corresponding osmium complex [22]. This is a convenient starting material for extending the chemistry of osmium ammines in low oxidation states, an opportunity that did not escape the attention of Allen and his co-workers [30,32,33]. The scope of the coordination chemistry of dinitrogen can be judged from a rather recent review by Sellmann [R12]. Even a cursory examination of the review paper will suffice to persuade the reader that the field of coordination chemistry has been greatly enriched by exploiting the properties of dinitrogen as a ligand.

Though this article is primarily an evaluation of Allen's scientific contributions, I cannot conclude without making an observation of a more personal nature. Even for those who did not know A.D. Allen in person, and who form their image of him solely from the published record, the fact that he was a gentleman as well as a scholar emerges clearly. He opened a field which attracted many able and imaginative co-workers and which became highly competitive, yet it was his unfailing grace to find merit in the contributions of others, even when these dealt with systems in the direct line of his own interests.

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