A Renaissance in Noble Gas Chemistry

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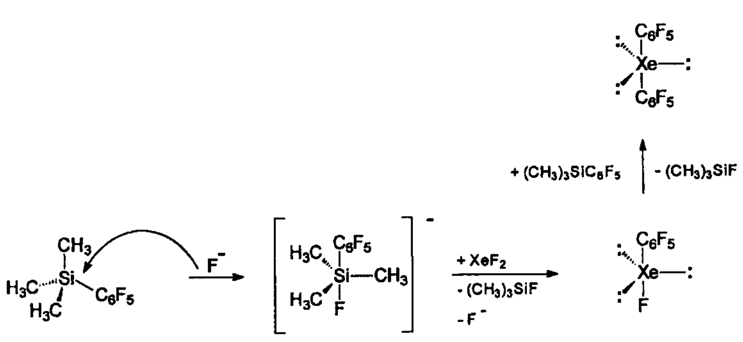
In spite of the predictions of stable noble gas compounds since at least 1902, unsuccessful attempts at their synthesis gave rise to the widely held opinion that noble gases are not only noble but also inert.[1] Thus, dogma-type statements to this effect could be found in practically every chemistry textbook and for a long time discouraged experimentalists from working in this area. It was not until 1962 that this dogma was shattered when Bartlett in Canada[2] published the first stable noble gas compound $XePtF_6$. This discovery triggered a worldwide frenzy in this area, and within a short time span many new xenon, radon, and krypton compounds were prepared and characterized. About 30 years and many publications later, new results in this area had slowed down to a trickle, and in the minds of most chemists the chapter on noble gas chemistry had been completed. A recent burst of startling discoveries, however, shows that noble gas chemistry is still full of surprises and may signal the beginning of a renaissance in this field.

The recent discoveries fall into four categories, and selected examples are given in the following paragraphs for recently published or ongoing research in these areas:

1) The formation of either new xenon(II)–heteroatom linkages or known xenon–heteroatom connectivities that involve higher oxidation states of xenon
2) The ability of XeF_2 to act as a ligand for numerous "naked" metal ions
3) The ability of xenon to act as a ligand
4) The observation of the first ground state argon compound containing covalent argon–heteroatom bonds

Formation of New Xe^{II}–Heteroatom Bonds

In the area of new Xe^{II}–heteroatom linkages the first examples of a C-Xe-C group have been prepared independently by two groups. Frohn's group at the University of Duisburg, Germany, synthesized first C_6F_5XeF from $[C_6F_5Xe]^+$ salts and $N(CH_3)_4F$ by metathesis and then converted it into $C_6F_5XeC_6F_5$ and C_6F_5XeCN by treating it with $[Cd(C_6F_5)_2]$ and $(CH_3)_3SiCN$, respectively.[3] In a different approach, Naumann's group at the University of Cologne, Germany, found that $C_6F_5XeC_6F_5$ and C_6F_5XeF are directly accessible from XeF_2 and $(CH_3)_3SiC_6F_5$ (Scheme 1).[4] Furthermore, Frohn and Schroer have recently obtained C_6F_5XeCl and $[C_6F_5XeClXeC_6F_5]^+$ (see Figure 1), two other interesting new compounds containing both Xe–C and Xe–Cl bonds.[5] These compounds are remarkable because, analogous to XeF_2, the have semi-ionic 3-center-4-electron bonds[6–8] that are only half as strong as the previously known, predominantly covalent, Xe–C and Xe–Cl bonds in the ions $[XeC_6F_5]^+$[9, 10] and $[XeCl]^+$,[5] respectively. Although the synthesis of CF_3XeCF_3 was already claimed in 1979,[11] all attempts to verify this claim have so far failed.[4]



Scheme 1. Synthesis of $C_6F_5XeC_6F_5$ and C_6F_5XeF from ref. [4].

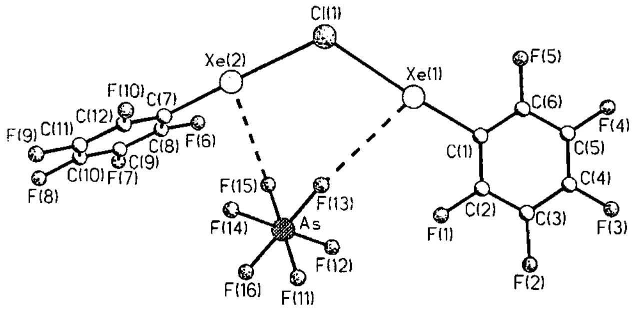


Figure 1. Molecular structure of $[C_6F_5XeClXeC_6F_5][AsF_6]$ from ref. [5].

A second example of a novel linkage involving Xe^{II} is the Xe-O-Xe bridge in the $[FXeOXeFXeF]^+$ ion discovered by Gerken and Schrobilgen at McMaster University[12] in part of a joint study with our group of the XeF^+/H_2O reaction system.[13]

Another first are the compounds involving Xe^{IV}–C bonds. From the reaction of XeF_4 with $C_6F_5BF_2$ the groups of Frohn and Zemva have successfully prepared and characterized the $[C_6F_5XeF_2]^+$ ion[14] that was also observed by Schrobilgen's group in the $XeF_6/C_6F_5BF_2$ reaction system.[15] Maggiarosa and Naumann have demonstrated a different approach toward the synthesis of a Xe^{IV}–C bond. By treating XeF_4 with the $[CN]^-$ ion they prepared the interesting $[XeF_4CN]^-$

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ion.[16] This anion is noteworthy because it is only the third example, after $[XeF_5]^{-}$[17] and $[IF_5]^{2-}$,[18] of a pentagonal planar AX_5-type species. Examples for Xe^{VI}–C bonds are still missing. This is not surprising, as the compatibility problems between a strongly oxidizing xenon fragment and a potential "fuel" ligand increase with increasing oxidation state and fluorine content of the xenon unit. Two promising approaches to overcome this problem involve the synthesis of anions rather than cations, because for a given oxidation state anions are weaker oxidizers than the corresponding cations, and the replacement of fluorine ligand pairs by doubly bonded oxygen atoms. The latter approach has been elegantly demonstrated by Schrobilgen's group for the synthesis of the first examples of the amazing Xe^{VI}–N and Xe^{VIII}–N bonds in the form of $O_3Xe{-}NCCH_3$, $F_4OXe{-}NCCH_3$, and $O_4Xe{-}NCCH_3$, respectively.[19]

In addition to the synthesis and characterization of the above compounds containing novel xenon connectivities, impressive progress was recently made in the characterization, by crystal structure determinations, of many previously known but poorly characterized noble gas compounds. Typical examples are $[KrF]^+$, $[Kr_2F_3]^+$, $[XeNHTeF_5]^+$, $[O_2XeF]^+$, $[F(XeO_2F)_2]^+$, and $[RCNXeF]^+$ salts by Schrobilgen et al.[20] and $[Xe_2]^+$ (Figure 2) by Seppelt's group from the Freie Universität in Berlin[21] that provided an opportunity to obtain an experimental bond length for the only known noble gas–noble gas bond. These studies provide much needed structural information, which helps us to understand the nature of these compounds.

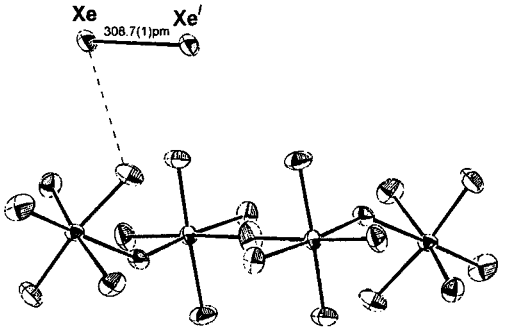

Figure 2. Molecular structure of $[Xe_2]^+[Sb_4F_{21}]^-$ from ref. [21].

XeF_2 as a Ligand for "Naked" Metal Ions

The second area of interest involves the recent exploitation by Zemva's group at the Jozef Stefan Institute in Ljubljana of a previous discovery in Bartlett's laboratory that XeF_2 can act as a fluorine-bridged ligand for Ag^I.[22] This discovery has been extended to numerous "naked" metal ions.[23] It is based on the reaction of metal $[AsF_6]^-$ salts in anhydrous HF solution with XeF_2. If the basicity of XeF_2 is intermediate between those of HF and the parent metal fluoride, XeF_2 can displace HF from the solvation sphere around the metal cation [Eq. (1)] without displacing the metal cation itself under formation of $[Xe_2F_3]^+$ salts [Eq. (2)]. In this manner, $[M(XeF_2)_m][AsF_6]_n$ salts have been isolated in which M can be Ag^I, Pb^{II}, Mg^{II}, Ca^{II}, Sr^{II}, Ba^{II}, or lanthanide(III); $m = 2-6$; for clarity the solvation of the other species by HF has been omitted from [Eqs. (1) and (2)]. A very interesting feature of these salts is the coordination around the metal ions. In the crystal structures determined so far, the metal ions coordinate to fluorine ligands from both XeF_2 and $[AsF_6]^-$ and exhibit high coordination numbers, typically 8 or 9, resulting in body-centered square antiprisms or trigonal prisms. Clearly, a systematic study of these types of adducts can provide a wealth of information on high coordination number chemistry.

$$[M(HF)_n]^{2+}[AsF_6]_2^- + m\,XeF_2 \rightarrow [M^{2+}(XeF_2)_m][AsF_6]_2^- + n\,HF \qquad (1)$$

$$[M(HF)_n]^{2+}[AsF_6]_2^- + 4\,XeF_2 \rightarrow 2\,[Xe_2F_3]^+[AsF_6]^- + n\,HF + MF_2 \qquad (2)$$

Xenon as a Ligand

The third area of interest results from the discovery by Seppelt's group that more than one xenon atom can attach itself to a metal center which in the case of gold leads to surprisingly stable Au–Xe bonds. Although weakly covalent bonding of a single noble gas atom to a metal center, such as Cu or Ag in their monohalides or Mn, Fe, Cr, Mo, or W in their pentacarbonyls, had been known, the bonding in $[AuXe_4]^{2+}$ involves 4(!) Xe ligands attached by relatively strong bonds to a single Au^{II} center in a square planar arrangement with a Xe–Au bond length of about 274 pm.[24] This discovery provides not only the first example of multiple xenon ligands but also represents the first strong metal–xenon bond. In view of the generally weak donor abilities of the noble gases, it remains to be seen if this type of coordination can be extended to other suitable transition metals.

The First Ground State Argon Compound with Covalent Argon–Heteroatom Bonds

The last subject of this highlight involves the work of Räsänen and co-workers at the University of Helsinki in Finland. By using low-temperature matrix-isolation spectroscopy, they have demonstrated not only the existence of numerous novel xenon– or krypton–heteroatom bonds, such as Xe–H, Xe–I, Xe–Br, Xe–S, Kr–H, Kr–C, and Kr–Cl,[25] but most significantly have provided experimental evidence for the first predominantly covalent, ground state argon–heteroatom bonds, Ar–H and Ar–F in the neutral H–Ar–F molecule.[26] Whereas weak van der Waals or excited state argon–heteroatom bonds had previously been known, vibrationally stable bonds in neutral ground state argon compounds were unknown. The HArF molecule appears to be stable only at very low temperatures in a matrix, and the energy barrier toward the 135 kcal mol^{-1} exothermic intramolecular elimination of HF was calculated to be only 8 kcal mol^{-1}. As pointed out by Frenking in a recent commentary,[27] the noble gas hydrogenfluoride molecules are only kinetically stable; their stability depends on the energy barriers toward decomposition which can be quite low, particularly in the condensed neat phase. Therefore, HArF is quite different from the many known Xe, Kr, and Rn compounds. Also, it should be kept in mind that there are no sharp boundaries between chemical bonds, charge transfer compounds,[28] and van der Waals complexes. In HArF, for example, the H–Ar bond has strong covalent contributions while the Ar–F bond is highly ionic. It is a human trait to put black-and-white labels on an universe consisting mainly of different shades of gray.

Does Räsänen's pioneering work suggest that we can expect to see in the near future the synthesis of marginally stable $[ArH]^+$, $[XeH]^+$ or $[ArF]^+$ salts as pure solids? Born–Haber cycle estimates show that solid $[ArH]^+[F]^-$ is about 130 $kcal\,mol^{-1}$ endothermic with respect to Ar and HF. Using the very strong Lewis acid SbF_5 to stabilize the ion as $[SbF_6]^-$, one can reduce the exothermicity of the decomposition reaction to about 70 $kcal\,mol^{-1}$. This value implies that a Lewis acid with an $[F]^-$ affinity that exceeds that of SbF_5 by at least 70 $kcal\,mol^{-1}$ would be required to render this reaction thermally neutral. This is beyond the current capabilities of Lewis acid chemistry.[29] The corresponding $[XeH]^+$ salt would be somewhat more favorable, but previous experiments from our laboratory to protonate Xe in HF/SbF_5 solution at −78°C were unsuccessful,[30] indicating that a Lewis acid stronger than SbF_5 is also required in this case. However, the bulk synthesis of marginally stable $[ArF]^+[XF]^-$ salts looks more promising, as was also concluded in a previous study.[31] Our Born–Haber cycle estimates indicate that $[ArF]^+[SbF_6]^-$ would be unstable by only 25 $kcal\,mol^{-1}$ relative to Ar, F_2, and SbF_5, and one can envision Lewis acids of a high enough $[F]^-$ affinity to achieve the goal of a marginally stable $[ArF]^+$ salt. However, even with a Lewis acid stronger than SbF_5 the synthesis would still present a major challenge because the ArF_2 parent molecule is vibrationally unstable. Therefore, any synthesis of $[ArF]^+$ salts will require synthetic methods analogous to those previously used for the syntheses of cations derived from nonexisting parent molecules, such as $[NF_4]^+$,[32, 33] which involve the use of elemental fluorine in combination with suitable activation energy sources.

This highlight shows that in spite of the relatively small number of laboratories involved in the ongoing efforts, significant breakthroughs have recently been achieved in noble gas chemistry, which heralds a renaissance in this field. In addition to the areas discussed above, one could envision the syntheses of compounds such as $[XeF_7]^+$, XeF_8, $[XeOF_5]^+$, $XeOF_6$, or KrF_4. With today's computational capabilities, the possible existence of these targets molecules should be reexamined and, if warranted, experimentally pursued.

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