A solid state intramolecular Wittig reaction enables efficient synthesis of endofullerenes including Ne@C\(_{60}\), \(^3\)He@C\(_{60}\) and HD@C\(_{60}\)

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Abstract: An open-cage fullerene incorporating phosphorous ylid and carbonyl group moieties on the rim of the orifice can be filled with gases (H, He, Ne) in the solid state, and the cage opening then contracted in situ by raising the temperature to complete an intramolecular Wittig reaction, trapping the atom or molecule inside. Known transformations complete conversion of the product fullerene to C\(_{60}\) containing the endohedral species. As well as providing an improved synthesis of large quantities of \(^4\)He@C\(_{60}\), H\(_2\)@C\(_{60}\) and D\(_2\)@C\(_{60}\), the method allows the efficient incorporation of expensive gases such as HD and \(^3\)He, to prepare HD@C\(_{60}\) and \(^3\)He@C\(_{60}\). The method also enables the first synthesis of Ne@C\(_{60}\) by molecular surgery, and its characterization by crystallography and \(^13\)C NMR spectroscopy.

Introduction

Compounds in which atoms or small molecules (A) are trapped in the cavity of cage fullerenes such as C\(_{60}\) are known as endofullerenes and denoted A@C\(_{60}\). They are of interest for study of their material properties and the properties of the isolated endohedral species.[1-6]

The noble gas endofullerenes of C\(_{60}\) have been the object of sustained theoretical studies[6-9] of their geometry, reactivity and electronic structure, and subject to a recent review.[3] Encapsulation of a noble gas in C\(_{60}\) was first detected by mass spectrometry in the formation of \(^4\)He@C\(_{60}\) from collision of accelerated C\(_{60}\) with helium gas,[4] and \(^4\)He@C\(_{60}\) was also observed at the part per million level in C\(_{60}\) formed by the carbon arc discharge method using He as the buffer gas.[5] High temperature and pressure exposure of C\(_{60}\) to the noble gases allows direct incorporation, and isolation of samples containing \(\sim 0.1\%\) of the endohedral atom He, Ne, Ar or Kr, or 0.03% of Xe.[8] Incorporation is improved by addition of KCN, to levels of 1% for He and \(\sim 0.3\%\) for Ar, Kr or Xe, albeit at the cost of lower recovery.[9-11] High energy helium bombardment of C\(_{60}\) under explosive conditions has also been used for direct encapsulation of the noble gas.[8] Removal of empty C\(_{60}\) using many cycles of preparative HPLC has been reported for the heavier noble gas endofullerenes (Ar@C\(_{60}\), 1.3 mg, 98% filled;[7c,9] Kr@C\(_{60}\), 0.14 mg, 90% filled;[10] Xe@C\(_{60}\) 0.32 mg, 50% filled[7b]), but direct encapsulation methods are not practical for synthesis of larger amounts of a noble gas endofullerene, and cannot be used to prepare molecular endofullerenes such as H\(_2\)@C\(_{60}\).

Yet, many applications exist to benefit from the availability of larger scale synthetic methods. Noble gas endofullerenes encapsulating the \(^3\)He or ^{129}\)Xe isotopes, with nuclear spin = \(\frac{1}{2}\), are potentially valuable as biosensors for detection by magnetic resonance, or as tools to monitor the course of fullerene reactions by NMR.[11a-d] Determining the quantised rotational and translational energy levels of an endohedral species, using inelastic neutron scattering and IR/THz spectroscopy, provides a powerful test of current models of non-bonding interactions.[12a-c] Endofullerenes in which a trapped molecule exhibits nuclear spin isomerism are of importance for the study of spin isomer interconversion, allotrope enrichment, and have potential applications to chemical and clinical magnetic resonance.[13] Here, nuclear spin conversion in H\(_2\)@C\(_{60}\)[14a-9] and H\(_2\)O@C\(_{60}\)[15a-b] has been studied to date.

![Figure 1. Open-cage fullerenes used in the reported syntheses of \(^4\)He@C\(_{60}\), H\(_2\)@C\(_{60}\), H\(_2\)O@C\(_{60}\) and HF@C\(_{60}\).](image-url)
To address these needs, a great deal of progress has been made in the synthesis of endofullerenes by multi-step routes (termed ‘molecular surgery’) in which a hole is chemically opened in the fullerene, an atom or small molecule enters the cavity, and the opening is then repaired to restore the original carbon cage with the atom or small molecule entrapped. Following the first insertion of He and H2 into an open fullerene by Rubin et al., cage closure was pioneered by Komatsu and Murata who reported syntheses of H2@C60 and 4He@C60 from open fullerene 1, by insertion of H2 directly into 1 (figure 1), and of 4He into the sulfoxide derivative, under high pressure (4He at 1230 atm, H2 at 800 atm) followed by a series of chemical reactions to re-form the C60 cage. The method allows larger scale synthesis of the noble gas endofullerene than is possible using direct encapsulation, 38 mg of 4He@C60 with 30% 4He filling was obtained. Similarly, the molecular endofullerene H2@C60 was prepared with 118 mg mass recovery and >90% H2 filling. Murata and co-workers also developed the synthesis and orifice-suture of open-cage fullerene 2 in their preparation of H2O@C60, and we have since reported an optimised procedure to obtain H2O@C60, and syntheses of H2@C60 and HF@C60 that also rely upon encapsulation of the endohedral molecule by 2. Recently, we used an open-cage fullerene with a larger opening to prepare Ar@C60 and CH3@C60. We now report a phosphorus ylid derivative of 2, that can be filled in the solid state and the orifice closed in situ by raising the temperature, enabling efficient synthesis of H2@C60 and 4He@C60, and their expensive isotopologues HD@C60, D2@C60 and 3He@C60, as well as the first ‘molecular surgery’ synthesis of Ne@C60.

Results and Discussion

Our reported synthesis of H2@C60 involved trapping of H2 inside open-cage fullerene 2. In this key step, 2 was formed in situ upon heating its hydrate, bis(hemiketal) 3, in solution with 3 Å molecular sieves under a high-pressure atmosphere of H2, to give H2@2 with 60% H2 incorporation. Then, heating H2@2 with Ph3P induced the first stage of ring-closure, giving H2@5, but also had to be conducted under a high-pressure of H2 to avoid loss of the endohedral molecule (scheme 1). We later showed that HF@3 undergoes dehydration and slow reaction with Ph3P at room temperature, to form a stable phosphorus ylid that is intermediate in the ring-closure leading to 5 but, unfortunately, only undergoes the necessary intramolecular Wittig reaction upon heating – leading to complete loss of HF. The structure of the phosphorus ylid, HF@4, was suggested by close agreement of a calculated 13C NMR spectrum of 4 with the experimental spectrum of the regioisomer shown in scheme 1, and we have now confirmed the structure of 4 by X-ray crystallography (figure 2). The crystal structure reveals that the C=O bond (1.223 Å) of the carbonyl group adjacent to the phosphorus ylid moiety is longer than those of the remote carbonyl groups (1.209 Å and 1.202 Å), suggesting that the ylid has substantial enolate character which may explain its good stability.

If entry of H2 or another species into 4 occurred at a temperature lower than that required for the intramolecular Wittig reaction, it would be possible to fill the ylid 4 then induce the Wittig reaction that traps the endohedral species simply by raising the temperature. This would avoid the need to vent gas, add Ph3P reagent, and re-pressureise as in our synthesis of H2@C60. Comparison of the activation enthalpies for entry of some small
At 160 °C closure of solid 4 was complete in less than 1 h, and heating the solid phosphorus ylid 4 under ~500 atm H2 at 160 °C gave H2@5 in 88 % yield with 80% encapsulation, demonstrating that endohedral incorporation of the gas is faster than ring closure in the solid state.

Open fullerenes have been filled in the solid state before,[17b–c,22a–c] but this is the first example where contraction of the cage opening can be carried out in situ, and there are huge practical advantages. The pressure-reactor can be small in volume, allowing higher pressures to be used safely, and the volume of gas needed to achieve the high pressure is much smaller – essential if the gas is expensive and/or rare (such as for encapsulation of 3He, see below). To apply this method of solid-state filling and in situ contraction for large scale synthesis, stainless steel pressure reactors with volumes between 1.2 – 5.0 mL and with pressure-ratings of 2400 – 4000 atm, were constructed as part of a bespoke apparatus for compression of gas using a manual intensifier (see Supporting Information). Results reporting the preparation of A@5, where A = Ne and isotopologues of H2 and He, are summarised in table 2, and described in detail below.

**H2@C60, HD@C60 and D2@C60**

HD@C60 is an interesting isotopologue of H2@C60 as it lacks the nuclear symmetry, and thus selection rules in the rotational energy levels. HD@C60 has been prepared before, and its IR and inelastic neutron scattering (INS) spectra acquired, but as a mixture with H2@C60 and D2@C60,[23a–b] Detailed predictions of the variable temperature INS spectra of HD@C60 have been made,[24] but to test them experimentally requires a large sample of pure material. Although the use of solid-state filling helps overcome the problem of the high cost of the gas, the low pressure (10 atm) at which HD is available limits the pressure our intensifier could generate to 80 – 85 atm. With an initial pressure of 82 atm HD gas at room temperature, heating with 4 at 160 °C for 2 h gave HD@5 with only 44% incorporation. The problem was alleviated by cooling the pressure reactor in liquid nitrogen before charging to 119 atm HD. Upon warming to room...
temperature, a pressure of 420 atm was achieved and at 140 °C, 520 atm. HD@5 was obtained in 75% yield and with an 83% filling factor of HD (table 2, entry 1). Of concern was the known disproportionation of HD to H2 + D2 in contact with iron. Under the described conditions, disproportionation was limited to <1%, but when higher temperatures and pressures were used for the filling / closure it became significant (after overnight exposure of 4 to 800 atm of HD at 180 °C, 35 % disproportion, as measured inside the cage, had occurred).

Similarly, cryogenic charging of the pressure-reactor enabled heating of phosphorus ylid 4 under 423 atm of D2 gas, or ~1800 atm of H2. Respectively, D2@5 was obtained with 73% filling and H2@5 with 95% filling, both in good yield (table 2, entries 2 and 3).

Closure of the cage opening of each compound, HD@5, D2@5 and H2@5 was carried out according to the two-step procedure previously reported (scheme 2). From a single high-pressure filling experiment we were easily able to prepare 100 – 150 mg of HD@C60 (83% filling), D2@C60 (73% filling) or H2@C60 (~95% filling), and obtain these endofullerenes on gram-scale over several batches.

4He@C60 and 3He@C60

Helium has much less favourable enthalpy of binding into open fullerene 4 than H2 (table 1) so a higher pressure is required for good incorporation. Our pressure intensifier has a limit of 1000 atm, but the cryogenic method described above enabled pressures well above 2000 atm to be generated in the reactor at a temperature of 180 °C. Filling and ring-contraction of 4 under almost 2400 atm of 4He lead to 50% helium incorporation in 4He@5 (table 2, entry 4) while, for comparison, 600 atm gave a filling factor of only 21%. Synthesis of 4He@C60 with 30% 4He encapsulation has been reported by Komatsu and Murata, although the method we describe in this paper is more easily scalable for preparation of the endofullerene in larger (gram) quantities. The rarity and expense of 4He has previously been an obstacle to the preparation of 4He@C60 – only 10 L at STP was available to us. So, a compressor was designed and built to minimise the dead volumes in our existing apparatus, and enabled 4He compression into a 2.4 mL capacity pressure reactor using the cryogenic charging method. This gave a pressure in excess of 2300 atm under an elevated temperature of >170 °C for the intramolecular Wittig reaction, and 4He@5 was obtained with 52% 4He filling (table 2, entry 5). Importantly, we were able to recover >99.8% of the 4He gas back into the apparatus and source cylinder after each experiment. Around 40% of the unrecovered gas had been encapsulated by the fullerene. Once again, conversion of He@5 to He@C60 was conducted as described in scheme 2, and >1 g material with ~50% filling was prepared for each isotope.

Ne@C60

The DFT calculations given in table 1 suggested that incorporation of Ne into 2 or 4 should be possible. The synthesis of Ne@C60 was first achieved by filling solid fullerene 2 (under Ne gas at 380 atm, 150 °C, 17 h), and isolation of the product as its hydrate, Ne@3. The filling factor of Ne@3 was estimated to be 15 – 20% from the 1H NMR spectrum. Although an attempt to convert Ne@3 to Ne@5 was made using the established method of heating with Ph3P at 120 °C, complete loss of neon occurred. Changing the conditions to PhP(2-furyl)a at 60 °C lead to isolation of Ne@5 without loss of endohedral neon, and Ne@C60 was subsequently obtained with 16% filling following the two-step procedure of scheme 2. Next, we examined the solid state filling and in situ ring-contraction of ylid 4 for preparation of Ne@5 with higher incorporation of neon. From exposure of 4 to 600 atm Ne at 160 °C for 2 h, Ne@5 was recovered with ~40% filling estimated from the high resolution ES+ mass spectrum by comparison of peak intensities for the filled and empty species. Furthermore, using the cryogenic method described earlier a pressure of >1700 atm could be attained, and a filling of 63% in Ne@5 was achieved (table 2, entry 6). As expected, Ne@C60 with the same filling factor of 63% was ultimately obtained, in 43% yield from Ne@5.

Ne@C60 has been previously prepared only using the direct insertion method, by heating C60 at high temperature and pressure with the gas, and resulting in unreported (small) quantities of material with 0.1 – 0.3% Ne incorporation. With 0.4 g in hand, we carried out enrichment of Ne@C60 (63% filled) to a sample with >99.5% incorporation of neon, by recycling preparative HPLC, and obtained a crystal structure of the nickel(II) octaethylporphyrin/benzene solvate, in which the C60 cage is indistinguishable from that of empty C60 (figure 3). The structure shows the neon atom at the centre of the cage.

In the noble gas@C60 series studied by 13C NMR spectroscopy to date, deshielding of the cage resonance with respect to empty C60 increases with the van der Waals radius of the entrapped atom: He@C60, Δδ = +0.02 ppm; Ar@C60, Δδ = +0.18 ppm; Kr@C60, Δδ = +0.39 ppm; and Xe@C60, Δδ = +0.96 ppm. Shown in figure 4(a), the 13C NMR resonance of Ne@C60 was measured with a chemical shift of δc = 142.83 ppm in 1,2-dichlorobenzene-d3 at 298 K, deshielded by Δδ = +0.024 ppm relative to empty C60. The absence of a visible peak for empty C60 attests to the high purity of the Ne@C60 sample, and displacement of the 13C peak of empty C60 by 23.6 ppm in the shielding (negative δ) direction, relative to the 13C peak of Ne@C60, was measured from a mixed sample of Ne@C60 and C60. The slight deshielding of the cage 13C resonance in Ne@C60 is within 1.2 ppm of that measured for He@C60 (Δδ = +0.025 ppm relative to C60), and is much less pronounced than in Ar@C60 and the heavier noble gas endofullerenes.
The methods described above allow the filling of large amounts of open-cage fullerene 4 with the various endohedral species described. Synthesis of bis(hemiketal) 3, the precursor to 4, is well described by Murata[28,29] but optimisation of the early cage-opening steps was necessary to more efficiently supply material for our scaled-up filling procedure (scheme 3). After opening the C60 cage by reaction with 3,6-bis(6-(tert-butyl)pyridin-2-yl)pyridazine,[30] the existing method for expanding the orifice by photo-oxygenation with singlet oxygen required irradiation of 6 in a mixture of CS2 (flashpoint ~30 °C, auto-ignition temperature 100 °C) and 1-chloronaphthalene, using a 500 W Xenon lamp as O2 is passed through the mixture over 23 h. Although recent improvements in both the reaction yield and safety have resulted from use of an LED light source and replacement of CS2 with CC14, a reaction time of 48 h is required (from 3 g C60).[30] We found that use of 2 molar equiv. of C60 (relative to the pyridazine reagent) in the first (cycloaddition) step gave a cleaner reaction – presumably by suppressing the formation of multiple addition products. Simple dilution of the product reaction mixture with toluene and direct transfer to the photoreaction vessel enabled the excess remaining C60 to serve as an efficient photosensitizer for the formation of 1O2, and the reaction time of photo-oxygenation was correspondingly reduced. Indeed, use of a 400 W high-pressure sodium lamp in a water-cooled immersion well, lead to completion of the photochemical reaction in just 1 h (on a scale using 10 g C60). Excess C60 was readily recovered during purification of 5 by column chromatography and the overall yield was 70%, based on the portion of C60 that was consumed in the reaction (see Supporting Information). Conversion of 5 to bis(hemiketal) 3 is carried out by oxidative cleavage using 4-methylmorpholine 4-oxide following the published procedure,[19] and 3 is converted to phosphorus ylid 4 upon treatment with 16 molar equiv. Ph3P at 60 °C.[19a] For this final step, an excellent and reproducible yield (85 – 90%) of 4 is achieved at multi-gram scale. Overall, the improved methods allow a 10 g batch of ylid 4 to be prepared in a few days.
Conclusion

Optimised synthesis and solid-state filling of a phosphorus ylid 4 with H₂, He or Ne, with in situ contraction of the cage opening via an intramolecular Wittig reaction, traps the gas inside. Large amounts of material can be processed in a small pressure reactor, allowing the use of high-pressure conditions and expensive gases. Further transformations gave up to 1 g each of endofullerenes He@C₆₀, He@C₇₀, Ne@C₆₀, Ne@C₇₀, Di@C₆₀, and Hd@C₆₀, which will enable experimental studies of these interesting species, for example using NMR, IR and inelastic neutron-scattering spectroscopy. These studies are underway. The new availability of a large quantity of He@C₆₀ offers the potential to extend its use in Magnetic Resonance Imaging, where ³He gas is already used to visualise air passages in the lung, by attachment to other species — although the development of methods for hyperpolarisation of the ³He nucleus will be needed to achieve this practical application. The first synthesis of pure HD@C₆₀ will permit the rotational and translational energy levels to be determined by INS, and compared with the established predictions as a test of these theoretical methods.

Synthesis of pure Ne@C₆₀ completes the series of noble gas endofullerenes to be prepared in macroscopic quantities (up to Xe@C₆₀). The absolute chemical shift, and relative endohedral translational energy levels to be determined by INS, and compared with the established predictions as a test of these theoretical methods.

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Keywords: endofullerene • NMR spectroscopy • synthetic methods • X-ray diffraction • phosphorus ylid

1. Optimal synthesis and solid-state filling of a phosphorus ylid 4 with H₂, He or Ne, with in situ contraction of the cage opening via an intramolecular Wittig reaction, traps the gas inside. Large amounts of material can be processed in a small pressure reactor, allowing the use of high-pressure conditions and expensive gases. Further transformations gave up to 1 g each of endofullerenes He@C₆₀, He@C₇₀, Ne@C₆₀, Ne@C₇₀, Di@C₆₀, and Hd@C₆₀, which will enable experimental studies of these interesting species, for example using NMR, IR and inelastic neutron-scattering spectroscopy. These studies are underway. The new availability of a large quantity of He@C₆₀ offers the potential to extend its use in Magnetic Resonance Imaging, where ³He gas is already used to visualise air passages in the lung, by attachment to other species — although the development of methods for hyperpolarisation of the ³He nucleus will be needed to achieve this practical application. The first synthesis of pure HD@C₆₀ will permit the rotational and translational energy levels to be determined by INS, and compared with the established predictions as a test of these theoretical methods.

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Solid state filling of a stable phosphorus ylid open-fullerene is followed by heating, inducing an in situ intramolecular Wittig reaction to reduce the size of the cage opening and trapping a single gas atom or molecule inside. Expensive gases can be compressed to high pressure, leading to high incorporation of the endohedral species. Cage closure steps allow preparation of gram-scale endohedral fullerenes including $^3$He@C$_{60}$, HD@C$_{60}$ and Ne@C$_{60}$. 