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Synthesis of homoleptic Re(I) complexes of isocyano-carboranes and the X-ray structure of hexakis(*p*-carboran-1-yl-isonitrile)Re(I)

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Abstract

Two homoleptic Re(I) complexes of *ortho* and *para*-carborane isocyanide ligands were prepared as the first examples of a new class of metal-based BNCT and BNCS agents. The target compounds were prepared in low yield through the reaction of $[Re_2(O_2CPh)_4Cl_2]$ and $[Re_2(OAc)_4Cl_2]$ with 3-isocyano-1,2-dicarba-*closo*-dodecaborane and a *para*-carborane azetidine derivative respectively. The desired product from the latter reaction was characterized crystallographically and is only the second reported molecular structure of a homoleptic Re(I) isonitrile complex.

Keywords: Carboranes; Isonitriles; Homoleptic; Rhenium; Technetium

1. Introduction

Boron neutron capture therapy (BNCT) [1,2] and synovectomy (BNCS) [3,4] are experimental binary treatment modalities for cancer and arthritis respectively [5]. A significant amount of research has been focused on designing BNCT agents that are capable of delivering substantial quantities of boron to cancer cells. Two of the most common strategies involve the conjugation of dicarba-*closo*-dodecaboranes to targeting agents and the inclusion of polyhedral boranes within drug delivery vehicles such as liposomes [6].

In order for BNCT to be a viable treatment strategy, the boron-targeting vehicle must deliver greater than 15 μg of ^{10}B per gram of tumor [7]. The BNCT agent must also clear from the blood and non-target tissues at a rate which is appreciably greater than the rate at which boron is lost from the tumor cells. In order to identify compounds possessing these characteristics some research groups have begun using clinical radioimaging techniques, such as positron emission tomography (PET) [8], as a means of evaluating BNCT agents in both humans and animal models. Direct observation of the biodistribution of new BNCT agents in animals has a number of advantages over conventional screening methods which involve measuring boron concentrations in excised tissue samples. These advantages include reduced subject to subject variability, the ability to carryout repeat studies in the same animal and the capacity to visualize the distribution of the BNCT agent in the entire animal. Animal imaging can also facilitates translational research in that the radiolabeled agent developed for the initial animal studies can subsequently be utilized for treatment planning exercises during human trials.

Because of the advantages of using radioimaging as a means of evaluating new delivery vehicles, we set out to design a novel class of BNCT/BNCS agents based on carborane complexes of rhenium. Such a system would enable us to substitute ^{99m}Tc, the most widely used radionuclide in diagnostic medicine [9], for rhenium

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without changing the basic structure of the agent under investigation. This latter point is particularly important, because the introduction of a foreign element (or chelate complex) can alter the distribution and pharmacokinetics of the compound under investigation.

As a model system, we chose the *para*-carborane (*p*-carborane) analogue of homoleptic isonitrile Re(I) complexes (Fig. 1). One of the reasons for selecting this particular compound is based on the fact that homoleptic ^{99m}Tc(I)–isocyanide complexes are used clinically for cardiac and tumour imaging consequently their stability in vivo has been well established [10]. A further attraction to the target compound as a BNCT/BNCS agent stems from its high boron content (60 boron atoms per molecule) and the fact that the compound can be made to target specific receptors through derivatization of the remaining carborane CH vertices.

2. Results and discussion

Previously we observed that dehydration of *N*-(1,12-dicarba-*closo*-dodecaboran-1-yl)formamide did not yield the desired 1-isocyano-*p*-carborane but gave the bis(imino)azetidine derivative **2** instead [11]. When compound **2** was reacted with $[Re(CO)_3(THF)_3]^+$ the hydrolysis product **3** was isolated and characterized crystallographically (Scheme 1). ESMS analysis of the reaction mixture from which **3** was isolated, revealed that a series of Re(I) isonitrile complexes having the general formula $[Re(CO)_x(L)_{6-x}]^+$ ($x = 0$–3, L = *p*-carborane isocyanide) also formed, albeit in very low yields [12]. These results prompted us to investigate the possibility of specifically preparing compound **1** using the azetidine **2** as a source of *p*-carborane isonitrile.

2.1. Reaction of compound 2 with $Re_2(OAc)_4Cl_2$

Following the general procedure for preparing homoleptic isonitrile Re(I) compounds developed by Walton and co-workers [13], an excess of the azetidine **2** was added to $Re_2(OAc)_4Cl_2$ [14] in methanol and the mixture heated to reflux (Scheme 2). TLC of the reaction indicated the presence of unreacted starting materials

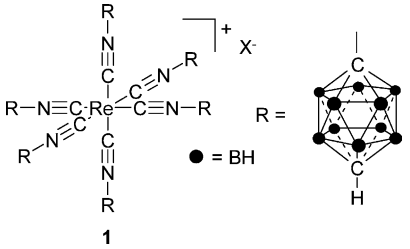
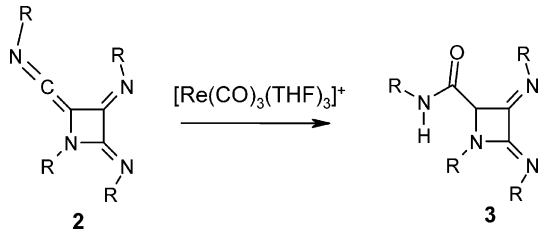


Fig. 1.



Scheme 1.

and the formation of a new compound, which was isolated by precipitation following ion exchange with KPF_6.

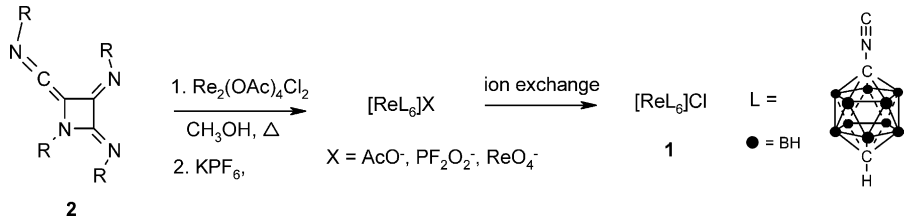
The positive ion ESMS of the new product shows only one major peak centered on an *m*/*z* value of 1201.6 which is consistent with the molecular mass and charge of **1**. This data was further supported by high resolution FABMS, which gave the precise mass and isotope distribution expected for the proposed target. The IR spectra of **1** exhibits peaks corresponding to the CH (3046 cm^{-1}), BH (2621 cm^{-1}) and CN groups (2091 cm^{-1}). The latter value is in close agreement with the CN stretching frequency reported for hexakis(phenyl isocyanide)technetium(I) [15]. The ^{1}H-NMR shows a singlet appearing at 3.31 ppm (CH) and a broad peak spanning 1.5–3.7 ppm, which is the archetypal signal observed for the hydrogen atoms bound to the cage boron atoms. The ^{13}C-NMR spectrum shows one very broad peak centered at 114.6 ppm, which suggests that the carborane substituents have unique orientations. In contrast, the ^{11}B{^{1}H} spectrum contains only two resonances at −11.7 and −15.1 ppm, which is consistent with a mono-substituted *p*-carborane derivative as a substituent in a homoleptic octahedral complex.

2.2. Solid state structure of compound 1

Air stable crystals of **1** were grown from an acetone solution at room temperature, and X-ray crystallography, using synchrotron radiation, confirmed that the isolated product was in fact the desired homoleptic complex (Fig. 2).

The Re(I) center is surrounded by a nearly octahedral arrangement of six *p*-carborane isonitrile ligands. The average Re–C distance, 2.030(6) Å, ranging from 2.015(6) Å (Re–C5) to 2.052(7) Å (Re–C6) (Table 1), is similar to the M–C distances reported for the one other published X-ray structure of a homoleptic isonitrile–Re(I) complex [16]. The average isonitrile bond distance in **1**, 1.166(8) Å, is also comparable to the distances reported for other related metal–isonitrile complexes [17].

The average Re–C–N bond angle in **1** is, as expected, essentially linear (176.7(5)°), ranging from 173.7(5) to 179.3(5)°. The orientations of the carborane substituents show remarkable variation spanning from 147.2(6) to



Scheme 2.

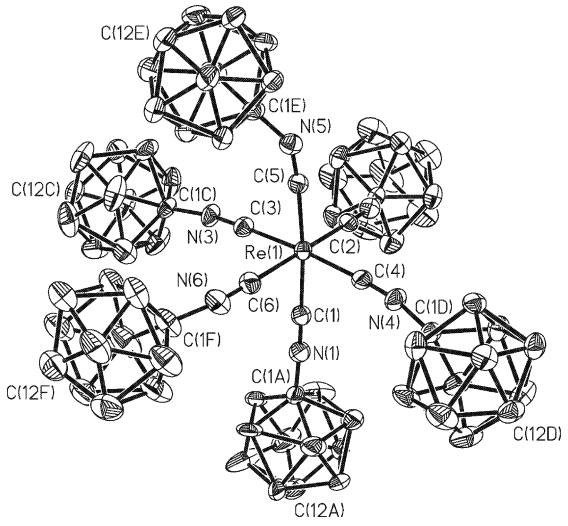


Fig. 2. ORTEP representation of **1** (ellipsoids shown at the 30% probability level). Hydrogen atoms and counter ions have been removed for clarity.

Table 1
Selected bond distances (Å) and bond angles (°) for compound **1**

Bond lengths			
Re(1)–C(1)	2.019(6)	Re(1)-C(2)	2.026(6)
Re(1)–C(3)	2.038(6)	Re(1)-C(4)	2.030(6)
Re(1)–C(5)	2.015(6)	Re(1)–C(6)	2.052(7)
C(1)–N(1)	1.197(8)	C(2)–N(2)	1.150(7)
C(3)–N(3)	1.165(7)	C(4)–N(4)	1.172(7)
C(5)–N(5)	1.175(8)	C(6)–N(6)	1.139(8)
N(1)–C(1A)	1.393(8)	N(2)–C(1B)	1.410(8)
N(3)–C(1C)	1.419(7)	N(4)–C(1D)	1.397(7)
N(5)–C(1E)	1.419(8)	N(6)–C(1F)	1.418(10)
Bond angles			
C(1)–N(1)–C(1A)	174.4(7)	C(2)–N(2)–C(1B)	156.1(6)
C(3)–N(3)–C(1C)	169.1(7)	C(4)–N(4)–C(1D)	169.0(6)
C(5)–N(5)–C(1E)	147.2(6)	C(6)–N(6)–C(1F)	164.0(7)
N(1)–C(1)–Re(1)	179.3(5)	N(2)–C(2)–Re(1)	173.7(5)
N(3)–C(3)–Re(1)	177.9(6)	N(4)–C(4)–Re(1)	176.7(5)
N(5)–C(5)–Re(1)	174.7(5)	N(6)–C(6)–Re(1)	177.9(6)

174.4(7)° (average C–N–C bond angle = 163.3(7)°). The angles at N2 (156.1(6)°) and N5 (147.2(6)°) are similar to the smallest bend angle in a recently reported homoleptic Cr(0) complex of isocyanoferrocene (157.2(2)°) [18].

Substantial bending at nitrogen in isonitrile–metal complexes is not unusual [19,21]. In $[Tc(CNtBu)_4(bpy)]PF_6$, for example, one of the isonitrile ligands trans to the bipyridine ligand shows a C–N–C angle of 148(2)° [20]. This type of bending is often attributed to donation of electron density from the metal to the ligand according to valence bond theory. For $M[(CN{-}tC_4H_9)_6]$ (M = Mo, Cr), a plot of decreasing C–N–C bending angle shows an approximately linear correlation with increasing M–C bond length [21]. The analogous plot for **1**, however, does not show the same relationship suggesting that the pronounced bending at N2 and N5 is most likely the result of packing effects associated with the bulky carborane ligand. It should also be noted that the M–C distances for **1** are similar to those for hexa(t-butylisonitrile) Re(I) and Tc(I) complexes [16] which do not exhibit bending at nitrogen of the magnitude reported here.

The six carborane cages in **1** were essentially symmetrical icosahedra with average B–B bond distances of 1.775(15) Å, ranging from 1.712(15) to 1.841(18) Å, while the average boron–carbon bond distance was 1.701(13) Å [22]. The solid-state structure of **1** contained three different counter ions: acetate, ReO_4^-, and $PF_2O_2^-$; the latter anion is an oxidative product of PF_6^-. The $PF_2O_2^-$ and ReO_4^- occupied the same crystallographic site in a 77:23 ratio, as determined by least-squares analysis (Table 2). The presence of the various counter ions were verified by negative ion ESMS. A second anion exchange using AMBERJET 4200 chloride ion-exchange resin enabled the complete conversion to chloride salt which was again confirmed by ESMS.

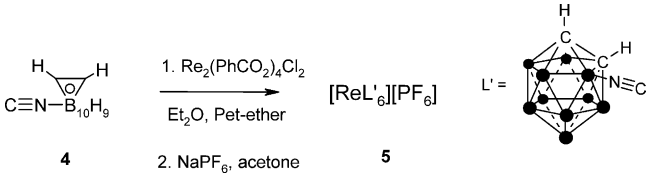
2.3. Synthesis of $[ReL'^6][PF_6]$ (L = 3-isocyano-1,2-dicarba-closo-dodecaborane)

In order to determine if the poor yield of **1** was associated with the low reactivity of compound **2**, the reaction was repeated using 3-isocyano-1,2-dicarba-*closo*-dodecaborane (L′) in place of the azetidine (Scheme 3). We have recently shown that this particular carborane ligand behaves like *t*-butyl isocyanide in that it reacts with $[NEt_3]_2[Re(CO)_3Br_3]$ to give $[Re(CO)_3L'^2Br]$ [12].

When compound **4** was reacted with $[Re_2(OAc)_4Cl_2]$ the desired product was detected only in trace quantities.

Table 2
Crystallographic data for compound **1**

Empirical formula	$C_{20}H_{66}B_{60}Cl_{2.31}N_6O_{3.69}P_{0.77}Re_{1.23}$
Formula weight	1433.07
Temperature (K)	97(2)
Wavelength (Å)	0.71535
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	
a (Å)	24.1564(19)
b (Å)	31.177(3)
c (Å)	21.1752(12)
α (°)	90
β (°)	94.706(4)
γ (°)	90
V (Å^3)	15894(2)
Z	8
D_{calc} (Mg m^{-3})	1.198
F(000)	5604
Absorption coefficient (mm^{-1})	2.002
Range of transmission factors	0.617926–1.000000
Crystal size (mm^3)	0.30 × 0.05 × 0.03
θ Range for data collection (°)	2.13–27.94
Index ranges	$-30 \le h \le 30$, $-40 \le k \le 40$, $-24 \le l \le 24$
Reflections collected	100033
Independent reflections	15290 [$R_{int} = 0.0737$]
Data/restraints/parameters	15290/0/848
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0662$, $wR_2 = 0.1744$
R indices (all data)	$R_1 = 0.0805$, $wR_2 = 0.1812$
Goodness-of-fit on F^2	1.555
Observed data [$I > 2\sigma(I)$]	12001
Largest difference peak and hole (e Å^{-3})	5.799 and −0.947



4 5

Scheme 3.

Thinking that the poor yield was a direct consequence of the incompatible solubilities of the starting materials, the Re compound was converted to the slightly more soluble benzoate complex [13]. The miscibility of the reactants improved to some extent, and as a result the desired product **5** was isolated in sufficient quantities to allow for detailed characterization. The yield of the reaction, unfortunately, was no better than for the reaction involving the azetidine suggesting that the poor yields maybe associated with the aforementioned solubility issues or as a result of the steric bulk of the carborane substituents.

The ESMS of the product shows a peak having a *m*/*z* value and isotopic distribution pattern consistent with the formation of the hexakis(isonitrile) complex **5**. High resolution FABMS confirmed that the major product had a formula corresponding to $[Re(L')_6]^+$. The IR spectra of **5** shows strong CH (3070 cm^{-1}), BH (2602 cm^{-1}) and CN stretches (2047 cm^{-1}) with the latter stretch being lower in energy than the ν(CN) value for **1** (2091 cm^{-1}). The ^{1}H NMR shows a broad signal corresponding to the B–H groups and a singlet at 5.10 ppm corresponding to the carborane CH groups. There are additional low intensity singlets in the vicinity of the CH peak which may indicate that there are different conformations of the complex in solution in which not all the carborane CH groups are equivalent. This is contrasted by the ^{13}C spectrum (75 MHz) which exhibits only one peak at 59.20 ppm. The ^{11}B{^{1}H} spectrum does not provide any additional insight into the structure of the complex as it contains particularly broad peaks at −1.99, −8.06 and −11.66 ppm. Despite repeated attempts, X-ray quality crystals of **5** could not be obtained.

3. Conclusions

In conclusion, two homoleptic Re(I) complexes of isocyano-carboranes were prepared albeit in poor yield. The X-ray structure of hexakis(*p*-carboran-1-yl-isonitrile)Re(I) was obtained conclusively demonstrating that azetidine **2** can, under the specified reaction conditions, act as a source of *p*-carborane isonitrile. We are currently exploring the mechanism of the reaction involving the azetidine while attempting to improve the yields of the reported reactions.

4. Experimental

4.1. Materials and procedures

All commercial reagents were used as supplied. Methanol was distilled from magnesium while ether was distilled from sodium/benzophenone. 3-Isocyano-*ortho*-carborane and the azetidine **2** were prepared following literature procedures [11,12]. Analytical TLC was performed on silica gel 60-F_{254} (Merck). Compounds containing *o*-carborane and *p*-carborane were visualized with 0.1 and 1% $PdCl_2$ in 3.0 M hydrochloric acid respectively, which upon heating gave dark brown spots. NMR spectroscopy experiments were performed on Bruker AV300 and DRX500 spectrometers. TMS and BF_3–Et_2O were used as internal standards for ^{1}H and ^{11}B spectra respectively. For NMR assignments, br refers to broad signals and s refers to singlets. Electrospray mass spectrometry experiments were performed on a Micromass Quattro Ultima instrument. Samples were dissolved in 50:50 $CH_3CN + H_2O$. IR spectra were run on a Bio-Rad FTS-40 FTIR spectrometer.

Single crystal X-ray diffraction data was collected by DND-CAT staff (SCrAPS, Advanced Photon Source, Argonne, IL) on the APS 5-ID-B beamline, equipped with a 20 mm Al filter and a MAR charge coupled device (CCD) (165 mm) using monochromatic synchrotron radiation ($\lambda = 0.71535$ Å). The single crystal of compound 1 was mounted on the tip of a glass fiber and the experiment carried out at 100 K, using a narrow frame acquisition (0.3°, 0.2 s/frame) in two hemispherical scans of 600 scans each. Accurate cell parameters were determined by a least-squares fit of the angular settings of the strong reflections, collected by a 12° scan in 40 frames over four different sections of reciprocal space (160 frames in total) using the SMART software [23]. Almost a complete sphere of data was collected to better than 0.8 Å resolution. Data reduction was carried out using the SAINT program [24], which applied a full (90°) polarization to the three-dimensionally integrated diffraction spots. The program SADABS [25] was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The structure was solved by using the direct-methods procedure in the Bruker SHELXTL program library [26], and refined by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms in all cases. All hydrogen atoms were assigned as fixed contributors at calculated positions with isotropic thermal parameters, based on the atom to which they were bonded. The ReO_4^- and $PF_2O_2^-$ anions were modeled with partial occupancy based on the amount of electron density observed in the difference map at the central atom (77% P and 23% Re).

4.2. Synthesis of [ReL$_6$][Cl] (L = 1-isocyano-1,12-dicarba-closo-dodecaborane) (**1**)

$[Re_2(OAc)_4Cl_2]$ (0.100 g, 0.148 mmol) and the azetidine **2** (0.212 g, 0.314 mmol) were dissolved in freshly distilled methanol (5.0 ml) giving a heterogeneous orange reaction mixture. The solution was brought to reflux for 72 h under Ar. The solvent was removed by rotary evaporation and the resulting green solid suspended in a saturated solution of KPF_6 in acetone for 1 h (5 ml). Upon removal of the acetone, the grey/green solid was stirred in ether (25 ml) for 2 h, the mixture filtered, and the filtrate concentrated in vacuo. The resulting solid was subsequently stirred in low boiling petroleum ether (25 ml) for 2 additional h whereupon the suspension was filtered and the filtrate evaporated to dryness. X-ray quality crystals were grown by the slow evaporation of a solution of the product in acetone.

To obtain the chloride salt the product was dissolved in 2:3 v/v water:THF and anion exchange performed using AMBERJET 4200(Cl^-) ion-exchange resin. Following filtration and evaporation, the resulting solid was dissolved in THF and the product precipitated through the addition of an equal portion of distilled-deionized water. The product was isolated as a yellow crystalline material. Yield: 10%. HR FABMS calculated for $C_{18}H_{66}B_{60}N_6Re$ 1202.091 m/z, found 1202.088 m/z. ESMS boron/Re isotopic distribution at 1201.6 m/z [M^+]. M.p. 167–169 °C (decomp.). ^{1}H-NMR (500.13 MHz, acetone-d_6) δ 3.31 (s, 6H, CH), 3.7–1.5 (br, BH). ^{13}C NMR (75 MHz, acetone-d_6) δ 114.67 (br). ^{11}B{^{1}H} NMR (160.46 MHz, acetone-d_6) δ −11.71 (br s, 30B), −15.13 (br s, 30 B). IR (THF, cm^{-1}): 3040, 2621, 2091.

4.3. Synthesis of [ReL′^{6}][PF$_6$] (L′ = 3-isocyano-1,2-dicarba-closo-dodecaborane) (**5**)

$[Re_2(O_2CPh)_4Cl_2]$ (0.152 g, 0.164 mmol) and compound **4** (0.168 g, 0.994 mmol) were suspended in freshly distilled diethyl ether (5.0 ml) and low boiling petroleum ether (0.5 ml) giving an orange heterogeneous reaction mixture. The solution was brought to reflux under Ar for 24 h. The solvents were removed by rotary evaporation and the resulting green solid suspended in a saturated acetone solution of KPF_6 for 1 h (5 ml). Upon removal of the acetone, the grey/green solid was stirred in ether (25 ml) for 2 h and filtered, and then stirred in low boiling petroleum ether (25 ml) for 2 additional hours. The resulting solid was collected by filtration, dissolved in THF (1 ml) and the product, a white solid, was precipitated from the reaction mixture, upon the addition of an equal portion of distilled-deionized water. Yield: 7%. HRFABMS: Calc. 1202.091 for [$C_{18}H_{66}B_{60}N_6Re$], Found 1202.087. ESMS (positive ion): $m/z = 1202.5$ [ReL′^{6}]$^+$. M.p. 119–121 °C (decomp.). ^{1}H-NMR (acetone-d_6, 500 MHz): 5.25, 5.10, 4.90 (br s, CH), 3.01–1.50 (br, BH). ^{13}C-NMR (acetone-d_6, 75 MHz): 59.20. ^{11}B-NMR (acetone-d_6, 96 MHz): −1.99, −8.06, −11.66. IR (CH_2Cl_2, cm^{-1}): 3070, 2602, 2047.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 199281. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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