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Molecular construction based on icosahedral carboranes and aromatic *N*,*N*′-dimethylurea groups. Aromatic layered molecules and a transition metal complex

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Abstract

cis-Preference of *N*-methyl aromatic ureas in combination with regulation of the *C*-substituent on an *o*-carborane cage is applicable to construct structurally unique macromolecules. Aromatic ureas with multilayer structure (**5**–**12**) and an aromatic urea containing an intramolecular *nido*-carborane–cobalt complex (**13**) were synthesized and their structures were determined by X-ray crystallography. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The icosahedral carboranes (dicarba-*closo*-dodecaboranes) are chemical building blocks of high boron content, remarkable thermal and chemical stability, spherical geometry and exceptional hydrophobic character. Their unusual properties make them uniquely suitable for several specialized applications in the materials sciences and biomedical sciences. The high boron contents and chemical and thermal stability of the carboranes have been utilized in the preparation of thermostable polymers [1] and carrier molecules for boron neutron capture therapy [2]. The delocalization of 26 skeletal electrons in the cage has been utilized in the preparation of materials for liquid crystals [3] and nonlinear optics [4]. We have aimed to clarify their electronic properties in the field of physical organic chemistry [5] and to apply their spherical geometry and hydrophobic character in the field of medicinal chemistry [6].

Carboranes have also attracted interest as both guest and host molecules in the field of supramolecular chemistry [7]. Recent studies in this area include analyses of the effects of π-bonding interactions between cage CH and calix[5]arene [8], and hydrogen-bonding interactions between cage CH and diaza-18-crown-6 [9]. The construction of linear [10] and macrocyclic [11] molecules, in which carboranes are linked through organic groups or mercury atoms [12] has also progressed. The carboranes have several desirable features in this regard. Their rigid three-dimensional structures hold substituents in well-defined spatial relationships. The two carbon vertices of carboranes bear relatively acidic protons and readily allow substitution with metal and organic groups. Substituents can also be introduced at certain boron vertices.

We have reported on the conformational alteration caused by *N*-methylation of aromatic amides [13], guanidine [14] and ureas [15]. The *N*-methylamide group in these compounds exists in *cis*-orientation to the carbonyl group, both in the crystal and in solution, whereas the unsubstituted amide group exists in *trans*-orientation. Recently, we have reported the construction of aromatic molecules by utilizing the *cis*-preference of *N*-methyl aromatic ureas in combination with regulation of the *C*-substituent on the 1,2-dicarba-*closo*-dodecaborane (*o*-carborane) cage [16]. In spite of the bulkiness of the carborane cage, the *N*-methylated ureas

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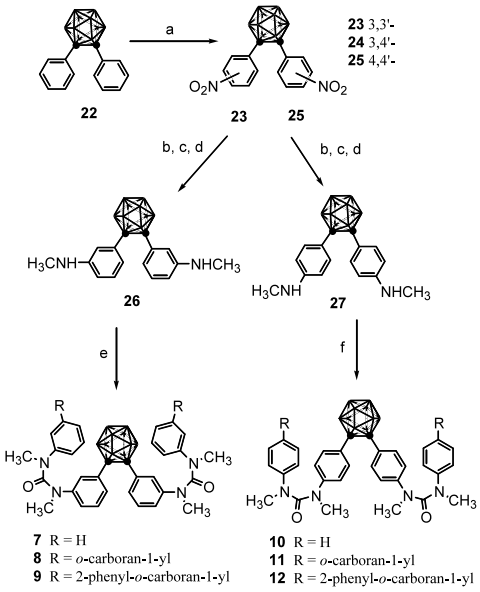
(**1**, **2**) exist in *cis*-conformation, both in solution and in the solid state. On the other hand, the secondary ureas (**3**, **4**) exist in *trans*-conformation [16]. We have also designed and synthesized macrocyclic compounds composed of 1,7-dicarba-*closo*-dodecaborane (*m*-carborane) moieties linked via their carbon vertices through *N*,*N*′-dimethyldiphenylurea groups as a new type of carboracycle [17]. These results were expected to be useful for construction of layered or helical molecules with both hydrophobic and hydrogen-bonding characters. We now report the application of the *N*,*N*′-dimethyl-*N*,*N*′-bis(carboranylphenyl)urea scaffold to design and synthesize aromatic ureas with multilayer structure (**5**–**12**) and an aromatic urea containing intramolecular *nido*-carborane–cobalt complex (**13**).

2. Results and discussion

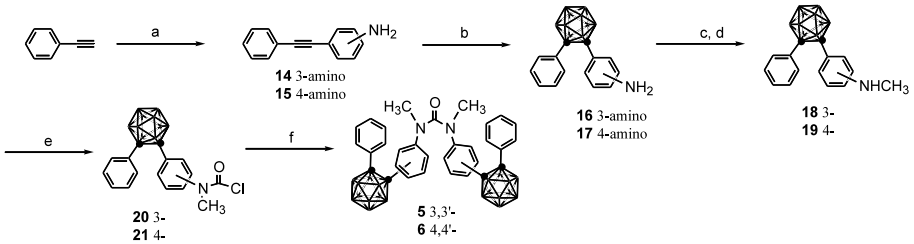
The syntheses of the designed molecules (**5**, **6**) with urea as a linking group are outlined in Scheme 1. 3-(**14**) And 4-phenylethynylaniline (**15**) were prepared by palladium-catalyzed coupling [18] of ethynylbenzene with 3- and 4-iodoaniline in 94–95% yields. Reaction of the phenylethynylanilines with decaborane (**14**) in acetonitrile–benzene under reflux for 3 days afforded 1-(3-aminophenyl)- (**16**) and 1-(4-aminophenyl)-2-phenyl-*o*-carboranes (**17**) in 27–28% yields. Formylation of the anilines (**16** and **17**) with formic–acetic anhydride followed by reduction gave the *N*-methylanilines (**18** and **19**) in 79–81% yields. The *N*-methyl anilines were transformed to the carbamoyl chlorides (**20** and **21**) by treatment with triphosgene in dichloromethane at room temperature in 56–73% yields. Coupling reaction of the carbamoyl chlorides with the *N*-methyl anilines (**18** and **19**) gave the desired *N*,*N*′-dimethylated aromatic ureas (**5** and **6**) in 54–89% yields. The syntheses of the designed molecules (**7**–**12**) with two ureas as linking groups are outlined in Scheme 2. Nitration of 1,2-diphenyl-*o*-carborane (**22**) afforded a mixture of three isomers (3,3′-, 3,4′ and 4,4′) [19] of 1,2-bis(nitrophenyl)-*o*-carboranes (**23** (40%), **24** (39%) and **25** (15%)). The 3,3′- (**23**) and 4,4′- (**25**) dinitro derivatives were converted to *N*-methylanilines (**26** and **27**) through a



Scheme 2. (a) $HNO_3/H_2SO_4/CH_2Cl_2$; (b) H_2, Pd-C/ethanol; (c) formic/acetic anhydride, THF; (d) BH_3/THF/THF; (e) *N*-methyl-*N*-phenylcarbamoyl chloride (for **7**) or *N*-methyl-*N*-(3-*o*-carboranyl)-phenylcarbamoyl chloride (**28**) (for **8**) or **20** (for **9**), triethylamine/1,2-dichloroethane, reflux; (f) *N*-methyl-*N*-phenylcarbamoyl chloride (for **7**) or *N*-methyl-*N*-(4-*o*-carboranyl)-phenylcarbamoyl chloride (**29**) (for **10**) or **21** (for **12**), triethylamine/1,2-dichloroethane, reflux.

sequence of catalytic hydrogenation, formylation and reduction in 68–74% yields. The 3,3′-substituted *N*-methylaniline (**26**) was allowed to react with two equivalents of *N*-methyl-*N*-phenylcarbamoyl chloride, *N*-methyl-*N*-(3-*o*-carboranyl)phenylcarbamoyl chloride (**28**) or the carbamoyl chloride described above (**20**) to afford the corresponding *N*,*N*′-dimethylated aromatic ureas (**7**–**9**) in 51–60% yields. Similarly, the 4,4′-substituted *N*-methylaniline (**27**) was converted to the corresponding *N*,*N*′-dimethylated aromatic ureas (**10**–**12**) in 44–76% yields, using *N*-methyl-*N*-phenylcarbamoyl chloride, *N*-methyl-*N*-(4-*o*-carboranyl)-phenylcarbamoyl chloride (**29**) or the carbamoyl chloride described above (**21**). All of the compounds synthesized were confirmed to have appropriate elemental analysis and NMR spectroscopic data.

The structures of the cyclic compounds were examined by ^{1}H-NMR (Table 1). The compounds with one



Scheme 1. (a) 3-Iodoaniline (for **14**) or 4-iodoaniline (for **15**), $Pd(PPh_3)_2Cl_2$, CuI, di-*iso*-propylamine; (b) decaborane (**14**), acetonitrile/benzene, reflux; (c) formic/acetic anhydride, THF; (d) BH_3/THF/THF; (e) triphosgene, triethylamine/1,2-dichloroethane; (f) **18** (for **5**) or **19** (for **6**), triethylamine/1,2-dichloroethane, reflux.

Table 1
^{1}H-NMR spectral data of the synthesized carborane-containing ureas

Compound (solvent)	Chemical shifts (ppm) of aromatic protons						
	On benzene ring attached to urea [a]				On benzene ring attached to *o*-carborane [b]		
	H_{o1}	H_{o2}	H_m	H_p	$H_{o'}$	$H_{m'}$	$H_{p'}$
5 ($CDCl_3$)	6.69	6.30	6.74	7.04	7.36	7.12	7.24
6 ($CDCl_3$)	6.47		7.09		7.44	7.19	7.44
7 ($CDCl_3$)	6.69	6.59-6.98	6.76	6.59-6.98			
	6.59–6.98 [c]	6.59–6.98 [c]	6.59–6.98 [c]	6.59–6.98 [c]			
8 ($CDCl_3$)	6.63–6.99	6.63–6.99	6.63–6.99	6.63–6.99			
9 ($CDCl_3$)	6.60, 6.65	6.41, 6.45	6.74, 6.77	6.92, 7.03	7.32	7.10	7.23
10 ($CDCl_3$)	6.61		7.10				
	6.67 [c]		6.95 [c]	6.95 [c]			
11 ($CDCl_3$)	6.62, 6.70		7.11, 7.15				
12 ($CDCl_3$)	6.52		7.12		7.43	7.12	7.27
N,*N*′-Dimethyl-*N*,*N*′-bis[3-(*o*-carboranyl)phenyl]urea, **1** (DMSO-d_6)	6.96	6.92	7.10	7.10			
N,*N*′-Dimethyl-*N*,*N*′-bis[4-(*o*-carboranyl)phenyl]urea, **2** ($CDCl_3$)	6.74		7.16				
N,*N*′-Dimethyl-*N*,*N*′-diphenylurea ($CDCl_3$)	6.76		7.04	6.93			

[a] H_{o1} means proton which is *ortho* to urea bond, H_{o2} means proton which is *ortho* to both urea bond and carborane, H_m means proton which is *meta* to urea bond, and H_p means proton which is *para* to urea bond.
[b] $H_{o'}$ means proton which is *ortho* to carborane, $H_{m'}$ means proton which is *meta* to carborane, and $H_{p'}$ means proton which is *para* to carborane.
[c] Protons on terminal benzene rings.

urea (**5** and **6**) exhibited a single signal of *N*-methyl protons, and the compounds with two ureas (**7**–**12**) exhibited two sets of *N*-methyl signals, indicating that these compounds have symmetrical structures or exist in rapid equilibrium. There was no significant change in the chemical shifts of any compound even at 203 K. Although the detailed conformations in solution were not examined, a comparison of the chemical shifts suggested that the urea bonds in these molecules are predominantly (*cis*, *cis*). The protons *ortho* to the urea bonds of **7**–**12** are observed at 6.41–6.70 ppm, which is similar to those of *N*,*N*′-bis[3-(*o*-carboran-1-yl)phenyl]-*N*,*N*′-dimethylurea (**1**, 6.96 and 6.30 ppm) or *N*,*N*′-bis[4-(*o*-carboran-1-yl)phenyl]-*N*,*N*′-dimethylurea (**2**, 6.74 ppm), having (*cis*, *cis*) conformation, and at significantly higher field than those of *N*,*N*′-bis[3-(*o*-carboran-1-yl)phenyl]urea (**3**, 7.75 and 7.51 ppm) or *N*,*N*′-bis[4-(*o*-carboran-1-yl)phenyl]urea (**4**, 7.33 ppm) with (*trans*, *trans*) conformation. These results are consistent with the hypothesis that the benzene rings attached to the urea bonds of these compounds lie face–face with each other.

Among the synthesized *N*,*N*′-dimethylated aromatic ureas, recrystallization of four compounds afforded single crystals suitable for X-ray crystallographic analysis. The crystal structures of compounds **5**, **6**, **7** and **10** are shown in Figs. 1 and 2. The compounds with a 1,3-disubstituted benzene moiety, **5** and **7**, form multilayer aromatic structures with *W*-shaped conformation, which would be forced by the *cis*-preference of *N*,*N*′-dimethyl aromatic urea and substituent orientation control of the *o*-carborane moiety. Compound **6** with a 1,4-disubstituted benzene moiety, exists in two crystallographically independent molecules in one asymmetric unit. Both of them retain *cis*-preference of the *N*-methylated aromatic urea. One molecule of **6** (molecule A) exists in a *W*-shaped multilayer structure. In the other molecule (molecule B), the two terminal benzene arms are twisted at about 120° (compared with molecule A) to form a conical shape. Some intramolecular or intermolecular aromatic–aromatic interaction may account for the stabilization of this structure. Unfortunately, compound **10** with a 1,4-disubstituted benzene scaffold did not for a multilayer structure. One of the urea bonds exists in (*cis*, *cis*) conformation, but the other possesses a (*cis*, *trans*) conformation. At present, it is not known whether its crystal structure is essentially more stable than the all-(*cis*, *cis*) conformation. These results indicate that the combination of an *o*-carboranyl moiety, rather than a 1,4-disubstituted aromatic urea moiety, and a 1,3-disubstituted aromatic urea moiety, favors aromatic multilayer conformation.

Another application, i.e. formation of a transition metal complex with *nido*-carborane derivatives derived from the *N*,*N*′-dimethyl-*N*,*N*′-dicarboranylphenylurea scaffold, was investigated. Removal of a boron atom from a *closo*-carborane using a strong nucleophile gives a *nido*-carborane $C_2B_9H_{12}^-$, as has been known for more than three decades [20]. These *nido*-anions are precursors to a large number of metallacarborane sandwich

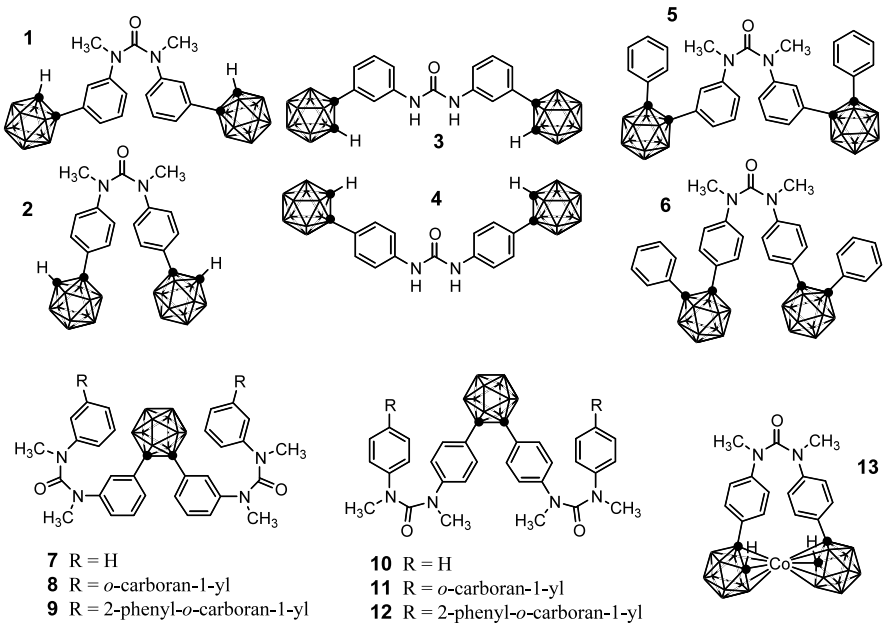


Fig. 1. Structures of the designed carborane-containing ureas (**5**–**13**).

compounds and heteroboranes [21]. We selected *N*,*N*′-bis[4-(*o*-carboran-1-yl)phenyl]-*N*,*N*′-dimethylurea (**2**) as a representative for study. Compound **2** was successfully converted into the bis(tetra-*n*-butylammonium) salt of the *nido*-derivative (**30**) by treatment with tetra-*n*-butylammonium fluoride [22] in 99% yield. The *nido*-carborane was subsequently transformed to *nido*-carborane–cobalt complex (**13**) by the use of potassium *tert*-butoxide as a base and anhydrous cobalt chloride in 25% yield. The crystal structures of compounds **30**, **13** and the parent compound **2** are shown in Fig. 3. Recrystallization of compound **30** from acetone–2-propanol afforded single crystals. The X-ray crystallographic analysis proved the absence of one boron

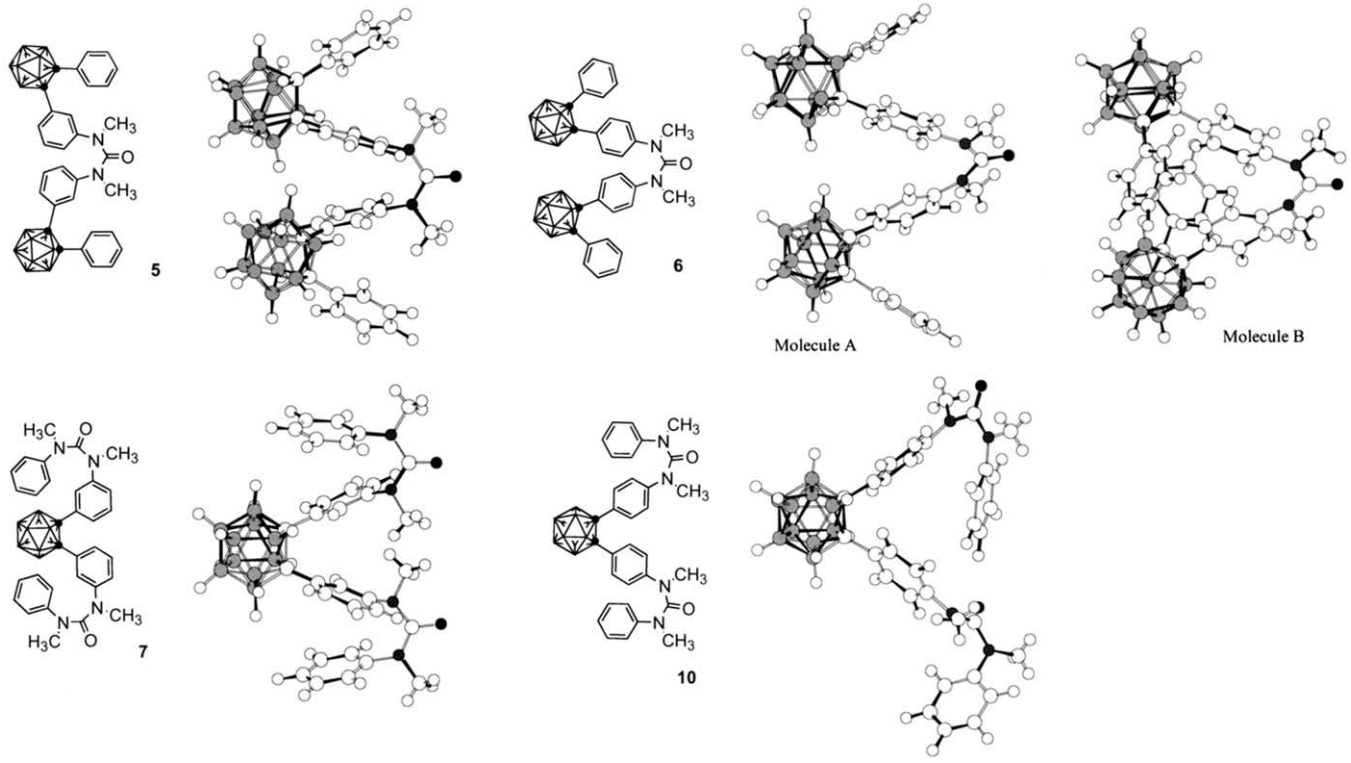


Fig. 2. Crystal structures of the carborane-containing ureas (**5**, **6**, **7** and **10**).

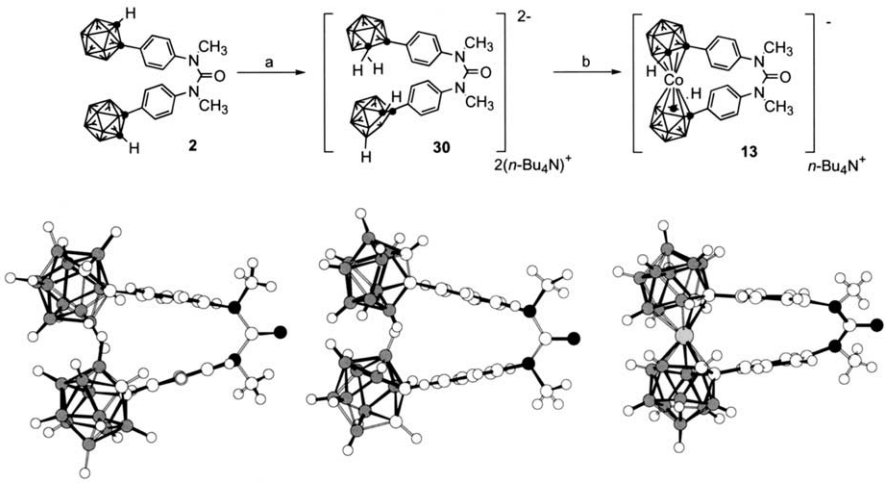


Fig. 3. Synthesis and crystal strutures of the carborane-containing ureas (**2**, **30** and **13**). (a) tetra-*n*-butylammonium fluoride/THF; (b) 1) potassium *t*-butoxide, 2) $CoCl_2$/dimethoxyethane.

Table 2
Dihedral angles between amide and phenyl planes of the ureas **2**, **30** and **13**

Compound	Dihedral angles between aromatic–aromatic planes	Ring center–ring center distance (Å)
2	24.5	3.71
30	25.3	3.67
13	15.7	3.10

vertex adjacent to the two carbon vertices of each carborane rings. This compound still exists in (*cis*, *cis*) conformation, like its parent compound **2**. Similarly, recrystallization of compound **13** from acetone–toluene gave single crystals. In the X-ray analysis, compound **13** has dl-configuration, and the two carborane moieties assembled with cobalt(III) ion in an intramolecular manner, which would be forced by the *cis*-preference of the parent compound that locks the molecular structure in a form suitable for intramolecular assembly.

Table 3
Crystal data of carborane-containing ureas **5**, **6**, **7** and **10**

Compound	**5**	**6**	**7**	**10**
Empirical formula	$C_{31}B_{20}H_{44}N_2O$	$C_{31}B_{20}H_{44}N_2O$	C_{32} $B_{10}H_{40}N_4O_2$	C_{32} $B_{10}H_{40}N_4O_2$
M_r	676.91	676.91	620.80	620.80
Recryst solvent	Diethyl ether	Diethyl ether	Diethyl ether	Diethyl ether
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Lacttice parameter				
a (Å)	11.4129 (11)	51.709 (3)	15.04 (2)	13.08 (2)
b (Å)	11.6471 (12)	11.3059 (6)	17.96 (3)	12.07 (2)
c (Å)	28.296 (3)	24.2328 (13)	7.017 (5)	21.705 (8)
α (°)			91.32 (7)	
β (°)		111.8850 (10)	93.33 (8)	95.43 (7)
γ (°)			68.41 (9)	
V (Å^3)	3761.3 (6)	13145.9 (11)	1759 (3)	3412 (7)
Space group	*Pbcn* (# 60)	*C*2/*c* (# 15)	$P\bar{1}$ (# 2)	$P2_1/c$ (# 14)
Z	4	12	2	4
ρ_{calc} (g cm^{-3})	1.195	1.208	1.172	1.208
μ (Mo–K$_\alpha$) (cm^{-1})	0.62	0.37	0.68	0.71
Temperature (°C)	-150 ± 1	23 ± 1	25 ± 1	25 ± 1
$2\theta_{max}$ (°)	56.9	46.6	50.2	50.1
Number of observations	2330 ($I > 3\sigma(I)$)	3713 ($I > 3\sigma(I)$)	2748 ($I > 2\sigma(I)$)	3742 ($I > 1.5\sigma(I)$)
Number of variables	245	1114	434	434
Goodness-of-fit (GoF)	1.02	0.43	2.00	1.88
Max. shift in cycle	0.39	1.60	0.012	0.011
Residuals: R, R_w	0.041, 0.047	0.042, 0.044	0.073, 0.083	0.078, 0.088
Max. peak in final difference map (e Å^{-3})	0.22	0.70	0.20	0.23

Table 4
Crystal data of carborane-containing ureas **30** and **13**

Compound	**30**	**13**
Empirical formula	$C_{19}B_{18}H_{36}N_2O$ $2(C_4H_9)_4N\cdot C_3H_6O$	$C_{19}B_{18}H_{34}N_2OCo$ $(C_4H_9)_4N\cdot C_7H_8$
M_r	1046.12	894.62
Recrystal solvent	Acetone–2-propanol	Acetone–toluene
Crystal system	Triclinic	Triclinic
Lattice parameter		
a (Å)	10.8717 (11)	10.6489 (13)
b (Å)	14.689 (2)	14.496 (2)
c (Å)	22.730 (3)	17.914 (2)
α (°)	99.806 (4)	997.005 (2)
β (°)	100.941 (4)	98.847 (2)
γ (°)	107.725 (4)	109.003 (2)
V (Å^3)	3292.2 (7)	2539.2 (5)
Space group	$P\bar{1}$ (# 2)	$P\bar{1}$ (# 2)
Z	2	2
ρ_{calc} (g cm^{-3})	1.051	1.170
μ (Mo–K$_\alpha$) (cm^{-1})	0.57	3.74
Temperature (°C)	-150 ± 1	-170 ± 1
$2\theta_{max}$ (°)	60.1	56.8
Number of observations	4037 ($I > 3.5\sigma(I)$)	6768 ($I > 3\sigma(I)$)
Number of variables	840	587
Goodness-of-fit (GoF)	2.58	1.28
Max. shift in cycle	4.24	9.63
Residuals: R, R_w	0.090, 0.094	0.046, 0.059
Max. peak in final difference map (e Å^{-3})	0.78	1.75

Selected structural parameters of the studied *nido*-carborane derivatives (**30** and **13**) and their parent compound (**2**) are listed in Table 2.

3. Conclusion

We synthesized several aromatic multilayered molecules based on the *cis*-preference of *N*-methyl aromatic ureas in combination with regulation of the *C*-substituent on the *o*-carborane cage. We also synthesized the *nido*-anion of *N*,*N*′-dimethyl-*N*,*N*′-bis(carboranylphenyl)urea and its transition metal complex utilizing the face–face conformation. The results described here should make it possible to develop a range of carborane-containing functionalized molecules that might find application in the fields of medicinal chemistry, materials science and supramolecular chemistry (Tables 3 and 4).

4. Experimental

4.1. General remarks

Melting points (m.p.) were obtained on a Yanagimoto micro hot stage without correction. Elemental analyses were carried out in the Microanalytical Laboratory, Faculty of Pharmaceutical Sciences, University of Tokyo, and were within $\pm0.3\%$ of the theoretical values. Thin layer chromatography (TLC) was conducted on Merck DC-platten Kieselgel 60F$_{254}$ (1.05715) with UV detection. ^{1}H-NMR spectra were recorded with a JEOL JNM-A500 spectrometer (500 MHz) or JEOL JNM-FX-400 spectrometer (400 MHz), with Me_4Si as an internal standard and chemical shifts are given in ppm as δ values from Me_4Si. THF was distilled over sodium benzophenone ketyl. Benzene was distilled over CaH_2 and stored over sodium wire.

4.2. X-ray crystallography

X-ray crystal structure analyses were performed on crystals selected compounds [23]. Diffraction data were obtained with a Rigaku AFC7S four-circle diffractometer and a Rigaku RAXISIIC imaging plate diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71070$ Å). Generally, indexing was performed from three oscillation which were exposed for 4 min, and a total of 15 oscillation images within the 2θ value of 50.0° were collected in the case of using the imaging plate area detector.

4.3. Synthesis of carboranylphenylureas **5**–**12**

4.3.1. 3-Phenylethynylaniline (**14**)

A solution of ethynylbenzene (4.5 g, 44.1 mmol), copper iodide (152 mg, 8 mmol), bis(triphenylphosphine)palladium (II) dichloride (1.12 g, 16 mmol) and diisopropylamine (16.2 g, 160 mmol) in THF (70 ml) was cooled in ice-bath. 3-Iodoaniline (8.8 mg, 40.2 mmol) was added, and the solution was stirred at room temperature (r.t.) for 1 h. After removal of the precipitate by filtration, the filtrate was diluted with EtOAc. The resultant solution was washed with water and brine. The solution was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane–ethyl acetate 8:1) to afford **14** as a brown liquid (7.4 g, 95%). ^{1}H-NMR ($CDCl_3$) δ 3.67 (br, s, 2H), 6.64 (m, 1H), 6.84 (t, $J = 2.0$, 7.8 Hz, 1H), 6.93 (d, $J = 2.0$ Hz, 1H), 7.11 (t, $J = 7.8$ Hz, 1H), 7.35–7.27 (m, 3H), 7.51–7.47 (m, 2H).

4.3.2. 4-Phenylethynylaniline (**15**)

Compound **15** was prepared from 4-iodoaniline (4.4 g, 20.1 mmol) in THF (70 ml) by the same method as used for preparation of **14**. Purification by silica gel column chromatography (eluent: *n*-hexane–ethylacetate 7:1) gave **15** as a brown solid (3.6 g, 94%). Recrystallization from *n*-hexane–CH_2Cl_2 gave brown flakes, m.p. 126–127 °C; ^{1}H-NMR ($CDCl_3$) δ 3.82 (br, s, 2H), 6.64

(d, $J = 8.5$ Hz, 2H), 7.35–7.28 (m, 5H), 7.50–7.48 (m, 2H).

4.3.3. 1-(3-Aminophenyl)-2-phenyl-1,2-dicarba-closo-dodecaborane (16)

A solution of decaborane (**14**) (1.3 g, 10.1 mmol), 3-phenylethynylaniline (**14**, 1.9 g, 10.0 mmol) and MeCN (6 ml) in dry C_6H_6 (60 ml) was refluxed under an argon atmosphere for 3 days. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: *n*-hexane–EtOAc, 4:1) to afford **16** as a yellow solid (858 mg, 28%). Recrystallization from *n*-hexane gave yellow flakes; m.p. 139–140 °C; ^{1}H-NMR ($CDCl_3$) δ 1.5–3.3 (br, m, 10H), 3.59 (br, s, 2H), 6.51 (dd, $J = 2.0$ and 7.9 Hz, 1H), 6.73 (t, $J = 2.0$ Hz, 1H), 6.78 (dd, $J = 2.0$ and 7.9 Hz, 2H), 6.87 (t, $J = 7.9$ Hz, 1H), 7.17–7.13 (m, 2H), 7.26–7.22 (m, 1H), 7.45–7.42 (m, 2H). Anal. Calc. for $C_{14}H_{21}B_{10}N$: C 53.99; H 6.80; N 4.50. Found: C 53.91; H 6.82; N 4.52%.

4.3.4. 1-(4-Aminophenyl)-2-phenyl-1,2-dicarba-closo-dodecaborane (17)

Compound **17** was prepared from decaborane (**14**) (718 mg, 5.9 mmol) and 4-phenylethynylaniline (**15**, 1.3 g, 6.5 mmol) by the same method as used for preparation of **16**. Purification by silica gel column chromatography (eluent: *n*-hexane–EtOAc 3:1) gave **17** as a yellow waxy solid (500 mg, 27%). Recrystallization from *n*-hexane gave yellow flakes; m.p. 169–170 °C; ^{1}H-NMR ($CDCl_3$) δ 1.5–3.3 (br, m, 10H), 3.82 (br, s, 2H), 6.64 (d, $J = 8.8$ Hz, 2H), 7.35–7.28 (m, 5H), 7.43 (d, $J = 8.6$ Hz, 2H). Anal. Calc. for $C_{14}H_{21}B_{10}N$: C 53.99; H 6.80; N 4.50. Found: C 54.28; H 6.90; N 4.40%.

4.3.5. 1-(3-N-Methylaminophenyl)-2-phenyl-1,2-dicarba-closo-dodecaborane (18)

A mixture of Ac_2O (840 mg) and formic acid (420 mg) was refluxed at 60–70 °C for 2 h. After the mixture had cooled, a solution of **16** (312 mg, 1.0 mmol) in THF (20 ml) was added, and the whole was stirred at r.t. for 3 h. After removal of solvent under reduced pressure, the residue was dissolved in EtOAc. The resultant solution was washed with water and brine. The solution was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane–EtOAc, 2:1) to afford 1-(3-formamidophenyl)-2-phenyl-1,2-dicarba-*closo*-dodecaborane as a white solid (83.5%). Recrystallization in *n*-hexane–CH_2Cl_2 gave colorless needles; m.p. 167–168 °C; ^{1}H-NMR ($CDCl_3$) δ 1.5–3.4 (br, m, 10H), 6.94–7.31 (m, 6H), 7.42–7.66 (m, 4H), 8.32–8.40 (m, 4H). Anal. Calc. for $C_{15}H_{21}B_{10}NO$: C 53.08; H 6.24; N 4.13. Found: C 53.35; H 6.08; N 3.97%. A 1.0 M BH_3–THF solution (2.5 ml, 2.5 mmol) was added carefully with ice cooling to a solution of the *N*-formylaniline in THF (10 ml) under an argon atmosphere. The resultant solution was stirred at r.t. for 8 h. Ten percent citric acid solution was carefully added and the resultant mixture was extracted with EtOAc. The combined organic extracts were washed with water and brine. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane–EtOAc, 2:1) to afford **18** as a pale yellow solid (252 mg, 94%). Recrystallization in *n*-hexane–CH_2Cl_2 gave pale-yellow flake 118–119 °C. ^{1}H-NMR ($CDCl_3$) δ 1.5–2.0 (br, m, 10H), 2.70 (s, 3H), 6.43 (dd, $J = 2.2$ and 7.9 Hz, 1H), 6.60 (t, $J = 2.2$ Hz, 1H), 6.73 (dd, $J = 2.2$ and 7.9 Hz, 1H), 6.90 (t, $J = 7.9$ Hz, 1H), 7.15 (m, 2H), 7.22–7.26 (m, 1H), 7.44 (m, 2H). Anal. Calc. for $C_{15}H_{23}B_{10}N$: C 55.36; H 7.12; N 4.30. Found: C 55.10; H 7.11; N 4.24%.

4.3.6. 1-(4-N-Methylaminophenyl)-2-phenyl-1,2-dicarba-closo-dodecaborane (19)

Compound **19** was prepared from **17** by the same method as used for preparation of **18**. Purification by column chromatography on silica gel (eluent: *n*-hexane–EtOAc 3:1) gave **19** as a pale yellow solid (81%, two steps). Recrystallization from *n*-hexane–CH_2Cl_2 gave pale-yellow flakes; m.p. 88–89 °C; ^{1}H-NMR ($CDCl_3$) δ 1.5–3.4 (br, m, 10H), 2.74 (d, 3H), 3.82 (br, s, 1H), 6.28 (d, $J = 8.8$ Hz, 2H), 7.24–7.13 (m, 5H), 7.44 (d, $J = 8.1$ Hz, 2H). Anal. Calc. for $C_{15}H_{23}B_{10}N$: C 55.36; H 7.12; N 4.30. Found: C 55.12; H 7.04; N 4.37%.

4.3.7. 1-(3-(N-Chloroformyl-N-methylamino)phenyl)-2-phenyl-1,2-dicarba-closo-dodecaborane (20)

A solution of Et_3N (83 mg, 0.8 mmol) in 1,2-dichloroethane (1 ml) was added dropwise to an ice-cooled solution of **18** (252 mg, 0.8 mmol) and triphosgene (83 mg, 0.3 mmol) in 1,2-dichloroethane (4 ml). Then the mixture was stirred at r.t. for 4 h. The resultant mixture was diluted with water and extracted with CH_2Cl_2. The combined organic phase was washed well with water and brine. The solution was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane–CH_2Cl_2, 2:1) to afford **20** as a colorless solid (217 mg, 76%). Recrystallization from *n*-hexane–CH_2Cl_2 gave colorless needles; m.p. 119–120 °C; ^{1}H-NMR ($CDCl_3$) δ 1.5–3.6 (br, m, 10H), 3.13 (s, 3H), 7.12–7.26 (m, 6H), 7.35–7.42 (m, 3H).

4.3.8. 1-(4-(N-Chloroformyl-N-methylamino)phenyl)-2-phenyl-1,2-dicarba-closo-dodecaborane (21)

Compound **21** was prepared from **19** (550 mg, 1.7 mmol) by the same method as used for preparation of **20**. Purification by column chromatography on silica gel (eluent: *n*-hexane–CH_2Cl_2, 1:1) gave **21** as a colorless solid (360 mg, 56%). Recrystallization from *n*-hexane–CH_2Cl_2 gave colorless needles; m.p. 128–129 °C; ^{1}H-

NMR ($CDCl_3$) δ 1.5–3.3 (br, m, B–*H*), 3.28 (br, s, 3H), 7.03 (d, $J = 7.2$ Hz, 2H), 7.13 (t, $J = 7.9$ Hz, 2H), 7.40 (d, $J = 7.9$ Hz, 2H), 7.26–7.22 (m, 1H), 7.46 (d, $J = 8.6$ Hz, 2H).

4.3.9. *N,N′-Bis[3-(2-phenyl-1,2-dicarba-closo-dodecaboran-1-yl)phenyl]-N,N′-dimethylurea (**5**)*

A mixture of the *N*-methylaniline (**18**, 110 mg, 0.3 mmol), the *N*-methyl-*N*-phenylcarbamoyl chloride (**20**, 110 mg, 0.3 mmol) and Et_3N (33 mg, 0.3 mmol) in 1,2-dichloroethane (20 ml) was refluxed for 72 h. The resultant mixture was diluted with water and extracted with CH_2Cl_2. The combined organic phase was washed well with water and brine. The solution was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane–EtOAc, 4:1) to afford **5** as a colorless solid (102 mg, 60%). Recrystallization from *n*-hexane–CH_2Cl_2 gave colorless needles; m.p. 259–260 °C; ^{1}H-NMR ($CDCl_3$) δ 1.5–3.2 (br, m, 20H), 2.81 (s, 6H), 6.30 (dd, $J = 1.8$ and 8.1 Hz, 2H), 6.69 (t, $J = 1.8$ Hz, 2H), 6.74 (t, $J = 8.1$ Hz, 2H), 7.04 (dd, $J = 1.8$ and 8.1 Hz, 2H), 7.12 (m, 4H), 7.21–7.26 (m, 2H), 7.36 (m, 4H). Anal. Calc. for $C_{31}H_{44}B_{20}N_2O$: C 55.01; H 6.55; N 4.11. Found: C 55.13; H 6.50; N 4.15%.

4.3.10. *N,N′-Bis[4-(2-phenyl-1,2-dicarba-closo-dodecaboran-1-yl)phenyl]-N,N′-dimethylurea (**6**)*

Compound **6** was prepared from **19** (110 mg, 0.3 mmol) and **21** (110 mg, 0.3 mmol) in 1,2-dichloroethane (20 ml) by the same method as used for preparation of **20**. Purification by column chromatography on silica gel (eluent: *n*-hexane–EtOAc, 3:2) gave **6** as a colorless solid (180 mg, 89%). Recrystallization from *n*-hexane–CH_2Cl_2 gave colorless needles; m.p. 193–194 °C; ^{1}H-NMR ($CDCl_3$): δ 1.4–3.4 (br, m, 20H), 2.87 (s, 6H), 6.47 (d, $J = 8.8$ Hz, 4H), 7.09 (d, $J = 8.8$ Hz, 4H), 7.18–7.21 (m, 4H), 7.26–7.30 (m, 2H), 7.43–7.45 (m, 4H). Anal. Calc. for $C_{31}H_{44}B_{20}N_2O$: C 55.01; H 6.55; N 4.11. Found: C 54.83; H 6.52; N 4.18%.

4.3.11. *Nitration of 1,2-diphenyl-1,2-dicarba-closo-decaborane*

A mixture of HNO_3 (61% w/w, 1.5 ml) and H_2SO_4 (97% w/w, 8.5 ml) was cooled in ice-bath. 1,2-Diphenyl-1,2-dicarba-*closo*-decaborane (**22**, 296 mg, 1.0 mmol) in CH_2Cl_2 (10 ml) was added, and the solution was stirred at r.t. for 3 h. The mixture was poured into ice-cold water (50 ml) and extracted with CH_2Cl_2. The combined organic phase was washed well with saturated $NaHCO_3$ solution and brine. The solution was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane–EtOAc, 8:1) to afford 1,2-bis(3-nitrophenyl)-1,2-dicarba-*closo*-dodecaborane (**23**) as a pale yellow solid (155 mg, 40%), 1,2-bis(4-nitrophenyl)-1,2-dicarba-*closo*-dodecaborane (**25**) as a pale yellow solid (59 mg, 15%), and 1-(3-nitrophenyl)-2-(4-nitrophenyl)-1,2-dicarba-*closo*-dodecaborane (**24**) as a pale yellow solid (150 mg, 39%). **23**: Recrystallization from *n*-hexane–CH_2Cl_2 gave pale-yellow needles; m.p. 216–217 °C; ^{1}H-NMR ($CDCl_3$) δ 1.6–3.4 (br, m, 10H), 7.42 (t, $J = 8.1$ Hz, 2H), 7.80 (dd, $J = 2.0$ and 8.1 Hz, 2H), 8.12 (dd, $J = 2.0$ and 8.1 Hz, 2H), 8.27 (t, $J = 2.0$ Hz, 2H). Anal. Calc. for $C_{14}H_{18}B_{10}N_2O_4$: C 43.52; H 4.70; N 7.25. Found: C 43.46; H 4.72; N 7.12%. **25**: Recrystallization from *n*-hexane–CH_2Cl_2 gave pale-yellow needles; m.p. 262–263 °C; ^{1}H-NMR ($CDCl_3$) δ 1.6–3.3 (br, m, 10H), 7.65 (d, $J = 9.2$ Hz, 4H), 8.04 (d, $J = 9.2$ Hz, 4 H). Anal. Calc. for $C_{14}H_{18}B_{10}N_2O_4$: C 43.52; H 4.70; N 7.25. Found: C 43.39; H 4.78; N 7.02%. **24**: Recrystallization from *n*-hexane–CH_2Cl_2 gave pale-yellow needles, m.p. 156–157 °C; ^{1}H-NMR ($CDCl_3$) δ 1.6–3.4 (br, m, 10 H), 7.42 (t, $J = 7.8$ Hz, 1H), 7.66 (d, $J = 9.0$ Hz, 2H), 7.77 (dd, $J = 2.2$ and 7.8 Hz, 1H), 8.04 (d, $J = 9.0$ Hz, 2H), 8.16 (dd, $J = 2.2$ and 7.8 Hz, 1H), 8.31 (t, $J = 2.2$ Hz, 1H). Anal. Calc. for $C_{14}H_{18}B_{10}N_2O_4$: C 43.52; H 4.70; N 7.25. Found: C 43.46; H 4.61; N 7.14%.

4.3.12. *1,2-Bis(3-N-methylaminophenyl)-1,2-dicarba-closo-dodecaborane (**26**)*

The nitro compound (**23**, 1.4 g, 3.7 mmol) in EtOH (150 ml) was hydrogenated over a catalytic amount of 10% Pd/charcoal until no more hydrogen was consumed. After removal of the catalyst by filtration, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane–EtOAc, 3:1) to afford 1,2-bis(3-aminophenyl)-1,2-dicarba-*closo*-dodecaborane as pale yellow flakes (1.1 g, 93%). Recrystallization from *n*-hexane–CH_2Cl_2 gave pale yellow flakes; m.p. 175–176 °C; ^{1}H-NMR ($CDCl_3$) δ 1.6–3.4 (br, m, 10H), 3.59 (br, s, 4H), 6.52 (dd, $J = 1.8$ and 7.8 Hz, 2H), 6.74 (t, $J = 1.8$ Hz, 2H), 6.78 (dd, $J = 1.8$ and 7.8 Hz, 2H), 6.88 (t, $J = 7.8$ Hz, 2H). Anal. Calc. for $C_{14}H_{22}B_{10}N_2$: C 51.51; H 6.79; N 8.58. Found: C 51.21; H 6.71; N 8.46%. The amine was converted to **26** by the same method as used for preparation of **18**. Purification by column chromatography on silica gel (eluent: *n*-hexane–EtOAc 2:1) gave **26** as a pale yellow solid (73%, two steps). Recrystallization from *n*-hexane–CH_2Cl_2 gave pale-yellow flakes; m.p. 110–111 °C; ^{1}H-NMR ($CDCl_3$) δ 1.7–3.4 (br, m, 16H), 3.64 (br, s, 2H), 6.44 (dd, $J = 2.0$ and 7.9 Hz, 2H), 6.62 (t, $J = 2.0$ Hz, 2H), 6.74 (dd, $J = 2.0$ and 7.9 Hz, 2H), 6.92 (t, $J = 7.9$ Hz, 2H). Anal. Calc. for $C_{16}H_{26}B_{10}N_2$: C 54.21; H 7.39; N 7.90. Found: C 54.24; H 7.48; N 7.70%.

4.3.13. 1,2-Bis(4-aminophenyl)-1,2-dicarba-closo-dodecaborane (27)

Compound **27** was prepared from **25** (1.35 g, 3.5 mmol) by the same method as used for preparation of **26**. Purification by column chromatography on silica gel (eluent: *n*-hexane–EtOAc, 1:1) gave 1,2-bis(4-aminophenyl)-1,2-dicarba-*closo*-dodecaborane as pale yellow flakes (1.1 g, 93%). Recrystallization from *n*-hexane–CH_2Cl_2 gave pale yellow flakes 202–203 °C; ^{1}H-NMR ($CDCl_3$) δ 1.5–3.5 (br, m, 10H), 3.73 (br, s, 4H), 6.38 (d, $J = 8.6$ Hz, 4H), 7.19 (d, $J = 8.6$ Hz, 4H). Anal. Calc. for $C_{14}H_{22}B_{10}N_2$: C 51.51; H 6.79; N 8.58. Found: C 51.43; H 6.81; N 8.46%. The amine was converted to **27** by the same method as used for preparation of **18**. Purification by column chromatography on silica gel (eluent: *n*-hexane–EtOAc 2:1) gave **27** as a pale yellow solid (80%, two steps). Recrystallization from *n*-hexane–CH_2Cl_2 gave pale-yellow flakes; m.p. 164–165 °C; ^{1}H-NMR ($CDCl_3$): δ 1.5–3.5 (br, m, 10H), 2.75 (d, 6H), 3.82 (br, s, 2H), 6.30 (d, $J = 7.0$ Hz, 4H), 7.23 (d, $J = 7.0$ Hz, 4H). Anal. Calc. for $C_{16}H_{26}B_{10}N_2$: C 54.21; H 7.39; N 7.90. Found: C 54.08; H 7.33; N 7.86%.

4.3.14. 1-(3-(N-Chloroformyl-N-methylamino)phenyl)-1,2-dicarba-closo-dodecaborane (28)

Compound **28** was prepared from 1-(3-*N*-methylaminophenyl)-1,2-dicarba-*closo*-dodecaborane (766 mg, 3.1 mmol) in 1,2-dichloroethane (15 ml) by the same method as used for preparation of **20**. Purification by column chromatography on silica gel (eluent: *n*-hexane–CH_2Cl_2, 3:2) gave **28** as a colorless solid (668 mg, 70%). Recrystallization from cyclohexane–Et_2O gave colorless needles; m.p. 98–99 °C; ^{1}H-NMR (acetone-d_6): δ 1.1–3.0 (br, m, 10H), 3.36 (br, s, 3H), 5.27 (br, s, 1H), 7.54 (br, m, 2H), 7.68 (br, s, 1H), 7.75 (br, s, 1H). Anal. Calc. for $C_{10}H_{18}B_{10}NClO$: C 38.52; H 5.82; N 4.49. Found: C 38.35; H 5.83; N 4.44%.

4.3.15. 1-(4-(N-Chloroformyl-N-methylamino)phenyl)-1,2-dicarba-closo-dodecaborane (29)

Compound **29** was prepared from 1-(4-*N*-methylaminophenyl)-1,2-dicarba-*closo*-dodecaborane (500 mg, 2.0 mmol) in 1,2-dichloroethane (15 ml) by the same method as used for preparation of **20**. Purification by column chromatography on silica gel (eluent: *n*-hexane–CH_2Cl_2, 3:2) gave **29** as a colorless solid (415 mg, 66%). Recrystallization from *n*-hexane–CH_2Cl_2 gave colorless needles; m.p. 98–99 °C; ^{1}H-NMR (acetone-d_6): δ 1.5–3.2 (br, m, 10H), 3.37 (br, s, 3H), 3.94 (br, s, 1H), 7.23 (d, $J = 8.6$ Hz, 2H), 7.53 (d, $J = 8.6$ Hz, 2H). Anal. Calc. for $C_{10}H_{18}B_{10}NClO$: C 38.52; H 5.82; N 4.49. Found: C 38.44; H 5.84; N 4.19%.

4.3.16. Compound 7

The *N*-methylaniline (**18**, 177 mg, 0.5 mmol), *N*-methyl-*N*-phenylcarbamoyl chloride (187 mg, 1.1 mmol) and triethylamine (111 mg, 1.1 mmol) in 1,2-dichloroethane (15 ml) was refluxed for 72 h. The resultant mixture was diluted with water and extracted with CH_2Cl_2. The combined organic phase was washed well with water and brine. The solution was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane–EtOAc, 1:1) to afford **7** as a colorless solid (140 mg, 51%). Recrystallization from *n*-hexane–CH_2Cl_2 gave colorless needles; m.p. 147–148 °C; ^{1}H-NMR ($CDCl_3$) δ 1.4–3.4 (br, m, 10H), 2.86 (s, 6H), 3.13 (s, 6H), 6.59–6.63 (m, 6H), 6.69 (t, $J = 1.8$ Hz, 2H), 6.75 (t, $J = 7.8$ Hz, 2H), 6.88–6.91 (m, 4H), 6.94–6.98 (m, 4H). Anal. Calc. for $C_{32}H_{40}B_{10}N_4O_2$: C 61.91; H 6.49; N 9.02. Found: C 61.81; H 6.62; N 8.86%.

4.3.17. Compound 8

Compound **8** was prepared from **18** (120 mg, 0.3 mmol) and **28** (227 mg, 0.8 mmol) in 1,2-dichloroethane (15 ml) by the same method as used for preparation of **7**. Purification by column chromatography on silica gel (eluent: *n*-hexane–EtOAc 1:1) gave **8** as a colorless solid (175 mg, 56%). Recrystallization from *n*-hexane–CH_2Cl_2 gave colorless needles; m.p. 281–282 °C; ^{1}H-NMR ($CDCl_3$) δ 1.4–3.4 (br, m, 30H), 2.88 (s, 6H), 3.14 (s, 6H), 6.63–6.66 (m, 4H), 6.69–6.72 (m, 2H), 6.83–6.86 (m, 4H), 6.94–6.98 (m, 6H). Anal. Calc. for $C_{36}H_{60}B_{30}N_4O_2$: C 47.77; H 6.68; N 6.19. Found: C 47.89; H 6.56; N 5.93%.

4.3.18. Compound 9

Compound **9** was prepared from **18** (57 mg, 0.1 mmol) and **20** (130 mg, 0.3 mmol) in 1,2-dichloroethane (5 ml) by the same method as used for preparation of **7**. Purification by column chromatography on silica gel (eluent: *n*-hexane–EtOAc 2:1) gave **9** as a colorless solid (102 mg, 60%). Recrystallization from *n*-hexane–CH_2Cl_2 gave colorless needles; 264–265 °C; ^{1}H-NMR ($CDCl_3$) δ 1.5–3.6 (br, m, 10H), 2.70 (s, 6H), 2.83 (s, 6H), 6.41 (dd, $J = 1.8$ and 8.0 Hz, 2H), 6.45 (dd, $J = 1.8$ and 8.0 Hz, 2H), 6.60 (t, $J = 1.8$ Hz, 2H), 6.65 (t, $J = 1.8$ Hz, 2H), 6.74 (t, $J = 8.0$ Hz, 2H), 6.77 (t, $J = 8.0$ Hz, 2H), 6.92 (dd, $J = 1.8$ and 8.0 Hz, 2H), 7.03 (dd, $J = 1.8$ and 8.0 Hz, 2H), 7.10 (t, $J = 7.8$ Hz, 4H), 7.20–7.26 (m, 2H), 7.32 (d, $J = 7.8$ Hz, 4H). Anal. Calc. for $C_{48}H_{68}B_{30}N_4O_2$: C 54.52; H 6.48; N 5.30. Found: C 54.48; H 6.43; N 5.25%.

4.3.19. Compound 10

Compound **10** was prepared from **19** (57 mg, 0.1 mmol) and *N*-methyl-*N*-phenylcarbamoyl chloride (126 mg, 0.7 mmol) in 1,2-dichloroethane (10 ml) by the same

method as used for preparation of **7**. Purification by column chromatography on silica gel (eluent: *n*-hexane–EtOAc 1:1) gave **10** as a colorless solid (160 mg, 76%). Recrystallization from *n*-hexane–CH_2Cl_2 gave colorless needles; m.p. 211–212 °C; ^{1}H-NMR ($CDCl_3$) δ 1.5–3.2 (br, m, 10H), 3.03 (s, 6H), 3.14 (s, 1H), 6.61 (d, $J = 8.6$ Hz, 4H), 6.67 (dt, $J = 7.0$ Hz, 4H), 6.91–6.99 (m, 6H), 7.10 (d, $J = 8.6$ Hz, 4H). Anal. Calc. for $C_{32}H_{40}B_{10}N_4O_2$: C 61.91; H 6.49; N 9.02. Found C 62.11; H 6.59; N 9.04%.

4.3.20. Compound **11**

Compound **11** was prepared from **19** (120 mg, 0.34 mmol) and **29** (227 mg, 0.75 mmol) in 1,2-dichloroethane (30 ml) by the same method as used for preparation of **7**. Purification by column chromatography on silica gel (eluent: *n*-hexane–EtOAc 3:2) gave **11** as a colorless solid (80 mg, 26%). Recrystallization from *n*-hexane–CH_2Cl_2 gave colorless needles; m.p. 170–171 °C; ^{1}H-NMR ($CDCl_3$) δ 1.5–3.3 (br, m, 30H), 3.04 (s, 6H), 3.08 (s, 6H), 3.84 (br, s, 2H), 6.62 (d, $J = 8.6$ Hz, 4H), 6.70 (d, $J = 8.6$ Hz, 4H), 7.11 (d, $J = 8.7$ Hz, 4H), 7.15 (d, $J = 8.6$ Hz, 4H). Anal. Calc. for $C_{36}H_{60}B_{30}N_4O_2$: C 47.77; H 6.68; N 6.19%. Found: C 47.89; H 6.56; N 5.93%.

4.3.21. Compound **12**

Compound **12** was prepared from **19** (85 mg, 0.2 mmol) and **21** (190 mg, 0.5 mmol) in 1,2-dichloroethane (20 ml) by the same method as used for preparation of **7**. Purification by column chromatography on silica gel (eluent: *n*-hexane–EtOAc 1:4) gave **12** as a colorless solid (140 mg, 55%). Recrystallization from *n*-hexane–CH_2Cl_2 gave colorless needles; m.p. 230–231 °C; ^{1}H-NMR ($CDCl_3$) δ 1.4–3.4 (br, m, 30H), 2.81 (s, 6H), 2.95 (s, 6H), 6.52 (t, $J = 8.4$ Hz, 8H), 7.10–7.15 (m, 12H), 7.25–7.29 (m, 2H), 7.43 (d, $J = 7.7$ Hz, 4H). Anal. Calc. for $C_{48}H_{68}B_{30}N_4O_2$: C 54.52; H 6.48; N 5.30. Found: C 54.36; H 6.48; N 5.20%.

4.4. Synthesis of transition metal complex with *nido*-carboranylphenylurea

4.4.1. *nido*-Carborane-containing urea **30**

Tetrabutylammonium fluoride solution (6 ml, 1.0 M in THF, 6 mmol) was added to a solution of *N*,*N*′-bis[4-(1,2-dicarba-*closo*-dodecaboran-1-yl)phenyl]-*N*,*N*′-dimethylurea (**2**, 260 mg, 0.5 mmol) in THF (5 ml), and the reaction mixture was stirred at r.t. for 3 h. The resultant mixture was then diluted with CH_2Cl_2 and washed well with water and brine. The solution was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford the crude *nido*-carborane derivative (**30**) as a white solid (482 mg, 99%). Recrystallization from EtOH gave colorless needles; m.p. 153–154 °C. ^{1}H-NMR ($CDCl_3$) δ 1.02 (t, $J = 7.3$ Hz, 24H), 1.41–1.50 (m, 16H), 1.61–1.70 (m, 16H), 2.30 (br, s, 2H), 3.03 (s, 6H), 3.13–3.21 (m, 16H), 6.46 (m, 4H), 6.94 (d, $J = 8.4$ Hz, 4H). Anal. Calc. for $C_{19}H_{36}B_{18}N_2O^{2-} \cdot 2(C_4H_9)_4N^+$: C 62.00; H 11.02; N 5.67. Found: C 62.15; H 10.84; N 5.63%.

4.4.2. Cobalt complex of *nido*-carboranylphenylurea **13**

nido-Carborane derivative (**30**, 100 mg, 0.1 mmol), potassium-*tert*-butoxide (115 mg, 1.02 mmol) and anhydrous cobalt(II) chloride (135 mg, 1.03 mmol) in 1,2-dimethoxyethane (10 ml) was refluxed under an argon atmosphere for 12 h. After cooling, the solvent was evaporated under vacuum, and the residue was redissolved in CH_2Cl_2. The resultant mixture was washed well with water and brine. The solution was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was then dissolved in a small amount of MeOH and treated with an excess of tetrabutylammonium hydrogensulfite in water. The orange–red precipitate was filtered off, washed well with water and finally purified by column chromatography on silica gel eluting with $CHCl_3$–MeOH (50:1) to afford the intramolecular *nido*-carborane cobalt complex (**13**) as a orange–red solid (20 mg, 25%). Recrystallization from *n*-hexane–acetone gave orange–red flakes; m.p. 269–270 °C. ^{1}H-NMR ($CDCl_3$) δ 1.02 (t, $J = 7.3$ Hz, 12H), 1.46–1.55 (m, 8H), 1.64–1.72 (m, 8H), 3.21–3.25 (m, 8H), 3.48 (d, 6H), 3.81 (br, d, 2H), 6.06 (m, 2H), 6.37 (m, 2H), 6.43 (m, 1H), 6.61 (m, 1H), 6.81 (m, 1H), 7.09 (m, 1H). Anal. Calc. for $C_{19}H_{34}B_{18}N_2OCo^- \cdot (C_4H_9)_4N^+$: C 51.39; H 8.79; N 5.24. Found: C 52.17; H 8.52; N 5.32%.

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[23] Crystallographic data for the new structures reported in this paper have been deposited with Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK. Ref. No. for **5** CCDC178142, for **6** CCDC178143, for **7** CCDC178144, for **10** CCDC178145, for **13** CCDC178146, for **30** CCDC178147.