Solvent–free synthesis of some triazole-based bis(N-heterocyclic carbene) ligands

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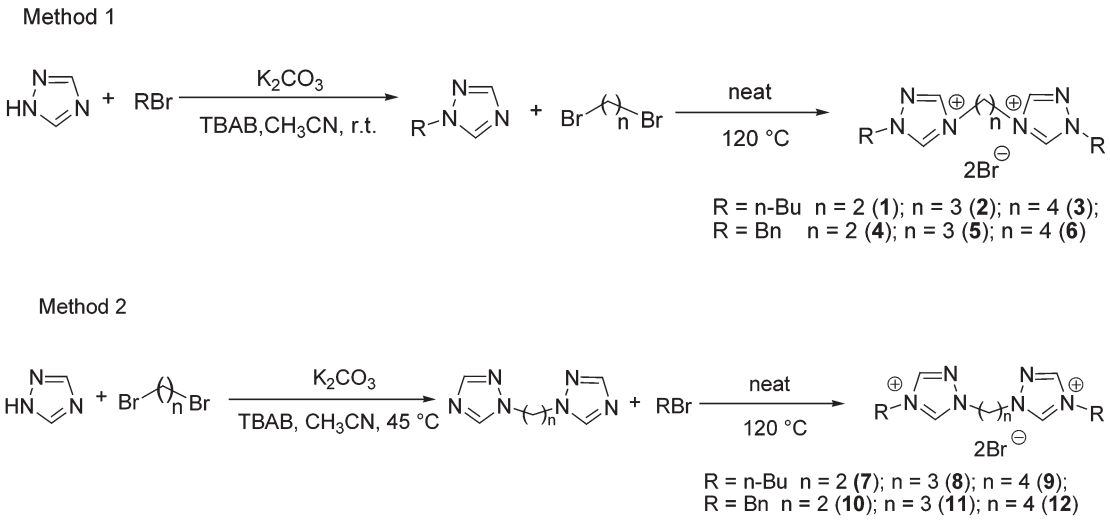
Two series of bistriazolium dibromides with different alkyl bridged length (*n* = 2–4) were synthesised through a simple solvent-free method. Six of these compounds were prepared from the reaction of 1-R-1H-1,2,4-triazole with dibromoalkane in moderate to excellent yield (45–98%). However, the other six compounds were prepared from the reaction of alkyl bridged bistriazole with bromoalkane in 55–99% yield. All compounds are new and were fully characterised by IR, NMR and elemental analyses.

Keywords: solvent free method, N-heterocyclic carbene ligand, bistriazolium dibromides

N-heterocyclic carbenes (NHCs) have proven to be versatile ligands in organometallic chemistry and catalysis.[1–5] Despite the large library of NHC ligands available, there are a relatively scarce number of such ligands containing triazole-based rings.[6–11] Triazolylidenes are an interesting class of NHCs because the presence of the three nitrogen atoms in the azole rings provides asymmetry and reduces the electron donation of the ligands. Furthermore, the asymmetric distribution of the nitrogens in the azole rings allows two different structures only by exchanging the position of the linkers between the azole rings and the terminal groups. We have been interested in the chemistry of bis-carbene ligands due to their higher stability to heat and air, and their improved catalytic performances. Previously, we have reported the synthesis of bis-NHC ligands based on imidazole,[12] and also developed a preparation of a series of imidazolium salts under solvent-free procedure.[13,14] As an extension to previous work, we now report the preparation of two series of triazole-based bis-NHC ligands under solvent-free conditions using 1H-1,2,4-triazole as a building block. Compared with conventional methods, this protocol features short reaction times, good yields, an eco-friendly process and easy control and handling.

Starting from 1H-1,2,4-triazoles, the two series of bistriazole salts were prepared in two ways (Scheme 1). In the first way, compounds **1**–**6** were synthesised by the reaction of 2 equiv. of N-alkyl triazoles which were generated from 1H-1,2,4-triazole, with dibromoalkanes. As both *N*-alkyl triazoles and dibromoalkanes are liquid at room temperature, completion of the reactions was easily monitored by the formation of solid compounds in the reaction mixture. The other way was that bridged bistriazoles generated from 1H-1,2,4-triazole reacted with 2 equiv. of bromoalkanes to produce compounds **7**–**12**. As bridged bistriazoles are melted at elevated temperatures, the reactions actually took place homogenously as well. In order to optimise the reaction conditions, the effects of reaction temperature were tested on compound **1** (Table 1, entries 1–6). The results showed that the better yield was obtained with higher temperature when the reaction was heated from 80 to 120 °C for 6 hours. For example, no product can be produced at 80 °C compared to 63% of yield at 120 °C. However, the yield was reduced at 130 °C probably due to a byproduct generated at high temperature. Then, the reaction was tested at 120 °C for an optimised reaction time (Table 1, entries 8–10). The results showed that the reaction could be completed within



Scheme 1 Synthesis of alkyl-bridged bis-triazolium dibromides.

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Table 1 Reaction conditions of alkyl-bridged bis-triazolium dibromides

Entry	Product	Temp. /°C	Time /h	Isolated yield /%
1	**1**	80	6	None
2	**1**	90	6	17
3	**1**	100	6	68
4	**1**	110	6	58
5	**1**	120	6	63
6	**1**	130	6	44
7	**1**	120	1	42
8	**1**	120	2	58
9	**1**	120	3	75
10	**1**	120	4	71
11	**2**	120	4	98
12	**3**	120	4	86
13	**4**	120	4	43
14	**5**	120	4	86
15	**6**	120	4	99
16	**7**	120	4	50
17	**8**	120	4	72
18	**9**	120	4	80
19	**10**	120	4	55
20	**11**	120	4	70
21	**12**	120	4	75

4 h. The reaction time was largely shortened to a few hours because of an enhancement in kinetics due to the high concentration of the reactants in the solvent-free conditions. Therefore, 120 °C and 4 hours were chosen for the rest of the reactions. The detailed reaction conditions and isolated yields of the products are shown in Table 1. The yield of products is higher with a bridged chain of three and four carbons between the triazoles.

In conclusion, we have demonstrated a solvent-free method to prepare various bistriazolium bromides. The advantages of this procedure are shorter reaction times, environmental friendliness, mild reaction conditions, and good yields.

Experimental

General procedures: All reagents were commercially available and were used without further purification. ^{1}H NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer at room temperature and referenced to the residual ^{1}H signals of the solvent. Coupling constants *J* are given in Hz. IR spectra were recorded on KBr pellets on a FTIR-Tensor 27 spectrometer. Melting points were detected by microscope melting point apparatus. Elemental analyses were performed on a EuroVektor Euro EA-300 elemental analyser. All compounds are unknown compounds, so they are fully characterised by IR, NMR spectroscopy and elemental analyses.

Typical procedure: Method 1: N-alkyl triazoles (2 mmol) and dibromoalkane (1 mmol) were heated to 120 °C for 4 h in a 10 mL Ace pressure tube. The complete change of the colourless solution to a white solid is the sign of the completion of the reaction. After completion, the reaction mixture was cooled to room temperature and was washed with acetone to give a pure product, which was dried under vacuum. Method **2**: N, N′-bridged bistriazoles (1 mmol) and bromoalkane (2 mmol) were heated to 120 °C for 4 h in a 10 mL Ace pressure tube. The complete change of the colourless solution to a white solid is the sign of the completion of the reaction. After completion, the reaction mixture was cooled to room temperature and was washed with acetone to give a pure product, which was dried under vacuum.

1,1′-Di-n-butyl-4,4′-(1,2-ethanediyl)bistriazolium dibromide (**1**): M.p. 265.6–266.1 °C. IR (KBr): 3105, 3041, 2958, 2874, 1575, 1460, 1394, 1238, 1160, 1074, 651, 627. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.43 (s, 2H, NC*H*N), 9.36 (s, 2H, NC*H*N), 4.93 (s, 4H, NCH_2N), 4.39 (t, *J* = 7.2 Hz, 4H, NCH_2), 1.84 (m, 4H, NCH_2CH_2), 1.30 (m, 4H, CH_2CH_3), 0.89 (t, *J* = 7.2 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.5, 142.8, 51.4, 46.4, 29.7, 18.6, 13.2. Anal. Calcd for $C_{14}H_{26}Br_2N_6$ (438.20 g mol^{-1}): C, 38.37; H, 5.98; N, 19.18. Found: C, 38.55; H, 5.83; N, 19.31%.

1,1′-Di-n-butyl-4,4′-(1,3-propanediyl)bistriazolium dibromide (**2**): M.p. 158.2–159 °C. IR (KBr): 3105, 3025, 2956, 2875, 1577, 1462, 1391, 1282, 1158, 1074, 694, 619. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.49 (s, 2H, NC*H*N), 9.43 (s, 2H, NC*H*N), 4.41 (m, 8H, NCH_2), 2.56 (m, 2H, $CH_2CH_2CH_2$), 1.86 (m, 4H, NCH_2CH_2), 1.32 (m, 4H, CH_2CH_3), 0.91 (t, *J* = 7.2 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.5, 142.6, 51.3, 44.2, 29.8, 28.5, 18.7, 13.2. Anal. Calcd for $C_{15}H_{28}Br_2N_6$ (452.23 g mol^{-1}): C, 39.84; H, 6.24; N, 18.58. Found: C, 39.57; H, 6.36; N, 18.44%.

1,1′-Di-n-butyl-4,4′-(1,4-butanediyl)bistriazolium dibromide (**3**): M.p. 157.5–159.7 °C. IR (KBr): 3113, 3028, 2956, 2873, 1576, 1454, 1386, 1156, 1073, 637, 619. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.51 (s, 2H, NC*H*N), 9.43 (s, 2H, NC*H*N), 4.38 (m, 8H, NCH_2), 1.85 (m, 4H, NCH_2CH_2), 1.93–1.82 (m, 4H, CH_2CH_2), 1.31 (m, 4H, CH_2CH_3), 0.91 (t, *J* = 7.2 HZ, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.5, 142.4, 51.3, 46.6, 29.9, 25.3, 18.6, 13.2. Anal. Calcd for $C_{16}H_{30}Br_2N_6$ (466.26 g mol^{-1}): C, 41.22; H, 6.49; N, 18.02. Found: C, 41.54; H, 6.27; N, 18.25%.

1,1′-Di-benzyl-4,4′-(1,2-ethanediyl)bistriazolium dibromide (**4**): M.p. 257–258 °C. IR (KBr): 3098, 3032, 2963, 2920, 2341, 1570, 1456, 1431, 1154, 1066, 726. 641. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.40 (s, 2H, NC*H*N), 9.31 (s, 2H, NC*H*N), 7.49–7.39 (m, 10H, ArH), 5.70 (s, 4H, Ar-CH_2), 4.90 (s, 4H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 145.0, 143.1, 132.9, 129.0, 128.9 128.8, 54.8, 46.6. Anal. Calcd for $C_{20}H_{22}Br_2N_6$ (506.24 g mol^{-1}): C, 47.45; H, 4.38; N, 16.60. Found: C, 47.31; H, 4.53; N, 16.77%.

1,1′-Di-benzyl-4,4′-(1,3-propanediyl)bistriazolium dibromide (**5**): M.p. 220–221 °C. IR (KBr): 3098, 3020, 2963, 2933, 2341, 1571, 1455, 1431, 1148, 1047, 716. 644. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.52 (s, 2H, NC*H*N), 9.41 (s, 2H, NC*H*N), 7.51–7.40 (m, 10H, ArH), 5.68 (s, 4H, Ar-CH_2), 4.43 (t, *J* = 7.2 Hz, 4H, CH_2), 2.55 (m, 2H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.9, 142.8, 133.0, 128.9, 128.8, 128.7, 54.7, 44.4, 28.4. Anal. Calcd for $C_{21}H_{24}Br_2N_6$ (520.26 g mol^{-1}): C, 48.48; H, 4.65; N, 16.15. Found: C, 48.67; H, 4.46; N, 15.91%.

1,1′-Di-benzyl-4,4′-(1,4-butanediyl)bistriazolium dibromide (**6**): M.p. 192.6–193.6 °C. IR (KBr): 3098, 3023, 2953, 2933, 2341, 1574, 1455, 1432, 1147, 725, 641. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.42 (s, 2H, NC*H*N), 9.33 (s, 2H, NC*H*N), 7.48–7.42 (m, 10H, ArH), 5.66 (s, 4H, Ar-CH_2), 4.34 (m, 4H, CH_2), 1.92 (m, 4H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.9, 142.7, 133.1, 128.9, 128.8, 128.7, 54.6, 46.7, 25.3. Anal. Calcd for $C_{22}H_{26}Br_2N_6$ (534.29 g mol^{-1}): C, 49.46; H, 4.90; N, 15.73. Found: C, 49.67; H, 4.69; N, 15.51%.

4,4′-Di-n-butyl-1,1′-(1,2-ethanediyl)bistriazolium dibromide (**7**): M.p. 218–219 °C. IR (KBr): 2929, 1818, 1584, 1524, 1423, 1574, 1167, 1072, 722, 624. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.41 (s, 2H, NC*H*N), 9.39 (s, 2H, NC*H*N), 5.00 (s, 4H, NCH_2), 4.30 (t, *J* = 7.2 Hz, 4H, NCH_2), 1.80 (m, *J* = 7.2 Hz, 4H, CH_2), 1.29 (m, 4H, CH_2), 0.90 (t, *J* = 7.2 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.8, 143.6, 49.7, 47.2, 30.6, 18.6, 13.2. Anal. Calcd for $C_{14}H_{26}Br_2N_6$ (438.20 g mol^{-1}): C, 38.37; H, 5.98; N, 19.18. Found: C, 38.62; H, 5.86; N, 19.29%.

4,4′-Di-n-butyl-1,1′-(1,3-propanediyl)bistriazolium dibromide (**8**): M.p. 188–190 °C. IR (KBr): 2961, 1818, 1577, 1523, 1455, 1159, 1074, 753, 625. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.43(s, 2H, NC*H*N), 9.37 (s, 2H, NC*H*N), 4.52 (m, 8H, NCH_2), 2.52 (m, 2H, CH_2), 1.84 (m, 4H, CH_2), 1.33 (m, 4H, CH_2), 0.90 (t, *J* = 7.2 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.6, 142.8, 48.3, 47.2, 30.6, 27.0, 18.7, 13.2. Anal. Calcd for $C_{15}H_{28}Br_2N_6$ (452.23 g mol^{-1}): C, 39.84; H, 6.24; N, 18.58. Found: C, 39.61; H, 6.15; N, 18.73%.

4,4′-Di-n-butyl-1,1′-(1,4-butanediyl)bistriazolium dibromide (**9**): M.p. 241.5–242.3 °C. IR (KBr): 2961, 1802, 1579, 1523, 1444, 1174, 1079, 673, 630. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.30 (s, 2H, NC*H*N), 9.30 (s, 2H, NC*H*N), 4.44 (m, 4H, NCH_2), 4.27 (m, 4H, NCH_2), 1.93 (m, 4H, CH_2CH_2), 1.83 (m, 4H, CH_2CH_2N), 1.30 (m, 4H, CH_2CH_3), 0.92 (t, *J* = 7.2 HZ, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.6, 142.5, 50.7, 47.2, 30.6, 24.7, 18.7, 13.2. Anal. Calcd for $C_{16}H_{30}Br_2N_6$ (466.26 g mol^{-1}): C, 41.22; H, 6.49; N, 18.02. Found: C, 41.50; H, 6.31; N, 18.19%.

4,4′-Di-benzyl-1,1′-(1,2-ethanediyl)bistriazolium dibromide (**10**): M.p. 229.2–230 °C. IR (KBr): 3095, 3039, 1953, 1816, 1578, 1496, 1416, 1315, 1211, 1143, 729, 695, 608. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.34 (s, 2H, NC*H*N), 9.39 (s, 2H, NC*H*N), 7.50–7.43 (m, 10H, ArH), 5.60 (s, 4H, Ar-CH_2), 4.98 (s, 4H, CH_2). ^{13}C NMR

(100 MHz, DMSO-d_6): δ = 144.8, 143.7, 133.4, 129.0, 128.6, 50.4, 49.8. Anal. Calcd for $C_{20}H_{22}Br_2N_6$ (506.24 g mol^{-1}): C, 47.45; H, 4.38; N, 16.60. Found: C, 47.67; H, 4.26; N, 16.33%.

4,4′-Di-benzyl-1,1′-(1,3-propanediyl)bistriazolium dibromide (**11**): M.p. 207.8.2–208.9 °C. IR (KBr): 3041, 1579, 1496, 1434, 1291, 1211, 729, 695, 608. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.44 (s, 2H, NC*H*N), 9.44 (s, 2H, NC*H*N), 7.57–7.42 (m, 10H, ArH), 5.60 (s, 4H, Ar-CH_2), 4.53 (t, J = 6.8 Hz, 4H, CH_2), 2.51 (m, 4H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.6, 142.9, 133.5, 128.9 128.8, 50.4, 48.5, 27.0. Anal. Calcd for $C_{21}H_{24}Br_2N_6$ (520.26 g mol^{-1}): C, 48.48; H, 4.65; N, 16.15. Found: C, 48.75; H, 4.78; N, 15.96%.

4,4′-Di-benzyl-1,1′-(1,4-butanediyl)bistriazolium dibromide (**12**): M.p. 242–243 °C. IR (KBr): 2984, 1820, 1584, 1498, 1421, 1373, 1152, 730, 701, 618. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.33 (s, 2H, NC*H*N), 9.38 (s, 2H, NC*H*N), 7.50–7.44 (m, 10H, Ar-*H*), 5.55 (s, 4H, Ar-CH_2), 4.43 (m, 4H, CH_2), 1.91 (m, 4H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.6, 142.6, 133.4, 129.0, 128.7, 50.8, 50.4, 24.7. Anal. Calcd for $C_{22}H_{26}Br_2N_6$ (534.29 g mol^{-1}): C, 49.46; H, 4.90; N, 15.73. Found: C, 49.72; H, 4.76; N, 15.56%.

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