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From straight chain to macrocyclic complexes containing mixed sulfur/nitrogen donors and coordinated 1,3-diynes

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Abstract

The acid-mediated reaction of $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}HOCH_2C{\equiv}C\text{–})\}_2]$ (**1**) with the *meta*- and *para*-substituted aminothiophenols, 3-NH_2–C_6H_4SH and 4-NH_2–C_6H_4SH, affords the straight chain species, $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}(3\text{-}NH_2\text{–}C_6H_4S)CH_2C{\equiv}C\text{–})\}_2]$ (**2**) and $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}(4\text{-}NH_2\text{–}C_6H_4S)CH_2C{\equiv}C\text{–})\}_2]$ (**3**), respectively. The molecular structure of **3** reveals the presence of two isomeric forms differing in the relative disposition of the *S*-aryl groups. Conversely, reaction of **1** with the *ortho*-substituted aminothiophenol, 2-NH_2–C_6H_4SH, furnishes the 10-membered macrocyclic species $[\{Co_2(CO)_6\}_2\{cyclo\text{-}\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}CH_2C_2C_2CH_2SC_6H_3\text{–}NH\text{-}2\}]$ (**4**) along with the linear chain complex $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}(2\text{-}NH_2\text{–}C_6H_4S)CH_2C{\equiv}C\text{–})\}_2]$ (**5**). On the other hand, treatment of **1** with the *ortho*-substituted mercaptopyridine, 2-SH–C_5H_4N, in the presence of HBF_4 gives the salt $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}(2\text{-}S\text{–}C_5H_4NH)CH_2C{\equiv}C\text{–})\}_2](BF_4)_2$ (**6a**) in good yield; work-up in the presence of base affords the neutral complex $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}(2\text{-}S\text{–}C_5H_4N)CH_2C{\equiv}C\text{–})\}_2]$ (**6b**). Single crystal X-ray diffraction studies have been reported on **3**–**5** and **6a**.

Keywords: Cobalt; Coordinated 1,3-diyne; Macrocycle; Straight chain; N–C bond formation; Nicholas reaction

1. Introduction

The application of Nicholas-type chemistry [1] to promote the formation of ring systems containing both alkynes and a variety of other donor units has been the subject of a number of studies [2–4]. In particular, butyne-1,4-diol-$Co_2(CO)_6$ complexes and its derivatives have served as highly effective precursors to cyclic assemblies [3,4], while the use of more extended substrates such as bis(propargyl alcohol)–$Co_4(CO)_{12}$ complexes has only in recent years come to the fore [5–7]. This has, in part, been stimulated by the relevance of the resulting materials to nanoscience [8], molecular sensors [9] and to natural products [2,5].

Recently, we have been interested in employing the conjugated 1,3-diynediol, $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}HOCH_2C{\equiv}C\text{–})\}_2]$ (**1**, Fig. 1), as a substrate in Nicholas chemistry and have demonstrated that substituted aromatics can act as compatible reaction partners for facilitating ring formation. Depending on the nature of the aromatic substitution pattern, ring closure by a dual *S*,*S*- [10], *C*,*C*- [11], *C*,*O*- [11] or *S*,*C*-centred [12] nucleophilic attack are all possible leading to macrocycles (or carbocycles) with ring sizes between eight and twenty-two atoms.

As an extension to this work, this note is concerned with targeting aromatic reagents that could facilitate *S*,*N*-centred ring closure. Specifically, the acid-mediated reaction of **1** with 2-, 3- and 4-aminothiophenols along with 2-mercaptopyridine is probed in this study. It is noteworthy that studies concerned with N–C coupling reactions employing primary amines in Nicholas chemistry remain, in their own right, scarce [13].

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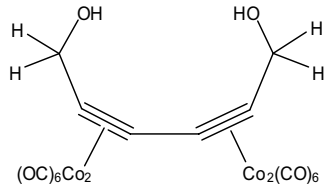


Fig. 1. Bis($Co_2(CO)_6$)-coordinated diyne-diol **1**.

2. Results and discussion

Reaction of [{$Co_2(CO)_6$(μ-η^2-$HOCH_2C{\equiv}C$–)}$_2$] (**1**) [14] with slightly greater than 2 equiv of *x*-NH_2–C_6H_4SH (*x* = 3, 4) in the presence of an excess of $HBF_4 \cdot OEt_2$ afforded, on work-up, [{$Co_2(CO)_6$(μ-η^2-(3-NH_2–C_6H_4S)$CH_2C{\equiv}C$–)}$_2$] (**2**) and [{$Co_2(CO)_6$(μ-η^2-(4-NH_2–C_6H_4S)$CH_2C{\equiv}C$–)}$_2$] (**3**) in moderate to high yield, respectively. Use of an equimolar ratio of the reagents also gave **2** and **3** but in lower yields. Complexes **2** and **3** have been characterised by mass spectrometry and by ^{1}H and ^{13}C NMR and IR spectroscopy (see Table 1 and Section 4). In addition, complex **3** has been the subject of a single crystal X-ray diffraction study.

Suitable crystals of **3** for the X-ray determination were grown from dichloromethane by slow diffusion of hexane at 0 °C. The molecular structure reveals that **3** exists as two geometric isomers (molecules A and B) one of which (B) contains a crystallographic centre of symmetry. Perspective views of molecule A (*cis*-aryls) and B (*trans*-aryls) are shown in Fig. 2a and 2b; selected bond lengths and angles for both molecules are listed in Table 2. Both isomers of **3** consist of a (4-NH_2–C_6H_4)$SCH_2C{\equiv}CC{\equiv}C$

Table 1
Selected characterisation data for the new complexes **2**–**6**

Complex	ν(CO)[a] (cm^{-1})	^{1}H NMR[b] (δ)	LSI mass spectrum
2	2101(s), 2082(s), 2060(vs), 2027(s)	7.11 (m, 2H, C_6H_4), 6.81 (m, 2H, C_6H_4), 6.74 (m, 2H, C_6H_4), 6.55 (m, 2H, C_6H_4), 4.48 (s, 4H, CH_2S), 3.69 (s, 4H, NH_2)	M^+–*n*CO (*n* = 2–4, 6–12)
3	2100(m), 2082(vs), 2060(vs), 2031(vs)	7.30 (d, 4H, C_6H_4, $^2J_{H-H}$ 8.4), 6.63 (d, 4H, C_6H_4, $^2J_{H-H}$ 8.4), 4.34 (s, 4H, CH_2S), 3.71 (s, 4H, NH_2)	M^+–*n*CO (*n* = 1–12)
4	2100(s), 2081(vs), 2059(vs), 2026(vs)	7.59 (d, 1H, C_6H_4, $^2J_{H-H}$ 7), 7.33 (t, 1H, C_6H_4, $^2J_{H-H}$ 7.0), 7.11 (d, 1H, C_6H_4, $^2J_{H-H}$ 8.0), 6.79 (t, 1H, C_6H_4, $^2J_{H-H}$ 7.0), 5.81 (t, 1H, N*H*, $^2J_{H-H}$ 7.0), 4.99 (d, 2H, CH_2NH, $^2J_{H-H}$ 7.0), 4.27 (s, 2H, CH_2S)	M^++H (772), M^+–*n*CO (*n* = 1–12)
5	2101(s), 2082(vs), 2060(vs), 2033(s), 2026(s)	7.45 (dd, 2H, C_6H_4, $^2J_{H-H}$ 7.7, $^3J_{H-H}$ 1.5), 7.14 (dt, 2H, C_6H_4, $^2J_{H-H}$ 8.0, $^3J_{H-H}$ 1.5), 6.74 (dd, 2H, C_6H_4, $^2J_{H-H}$ 8.0, $^3J_{H-H}$ 1.2), 6.71 (dt, 2H, C_6H_4, $^2J_{H-H}$ 7.7, $^3J_{H-H}$ 1.2), 4.35 (s, 4H, NH_2), 4.29 (s, 4H, CH_2S)	M^++H (897), M^+–*n*CO (*n* = 3–12)
6a	2099(w), 2080(s), 2058(vs), 2024(s)	11.0 (s, br, 2H, C_5H_4NH), 8.41–8.40 (m, 2H, C_5H_4NH), 7.56–7.54 (m, 2H, C_5H_4NH), 7.27–7.24 (m, 2H, C_5H_4NH), 7.00–6.98 (m, 2H, C_5H_4NH), 4.91 (s, 4H, CH_2)	M^+–BF_4 (957), M^+–$2BF_4$ (868), M^+–*n*CO (*n* = 3–12)
6b	2099(w), 2080(s), 2058(vs), 2024(s)	8.41–8.40 (m, 2H, C_5H_4N), 7.50–7.48 (m, 2H, C_5H_4N), 7.21–7.20 (m, 1H, C_5H_4N), 7.00 (m, 2H, C_5H_4N), 4.83 (s, 4H, CH_2)	M^++Na (892), M^+ (868), M^+–*n*CO (*n* = 3–12)

[a] Recorded in CH_2Cl_2 (apart from **6a** in THF) in 0.5 mm NaCl solution cells.
[b] ^{1}H NMR chemical shifts in ppm relative to $SiMe_4$ (0.0 ppm), coupling constants in Hz in $CDCl_3$ at 293 K.

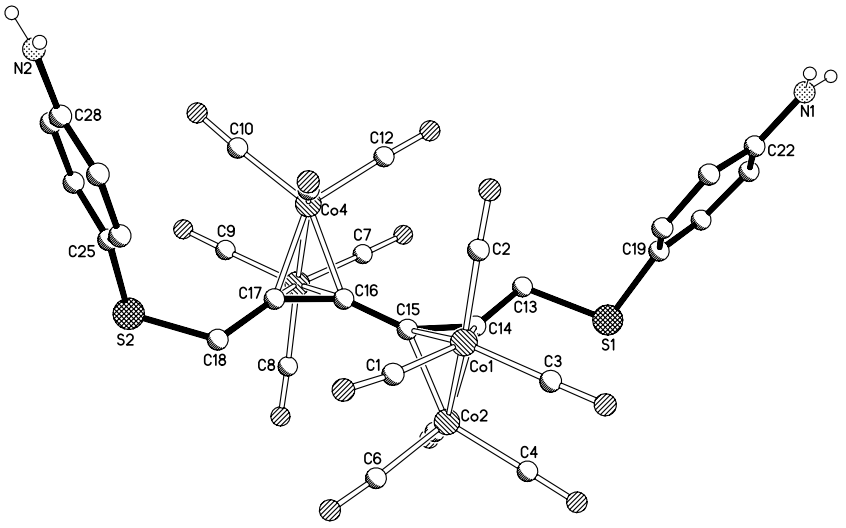


Fig. 2a. Molecular structure of **3** (molecule A: *cis*-aryls) with partial atom labeling scheme; all hydrogen atoms, apart from the amino hydrogens, have been omitted for clarity.

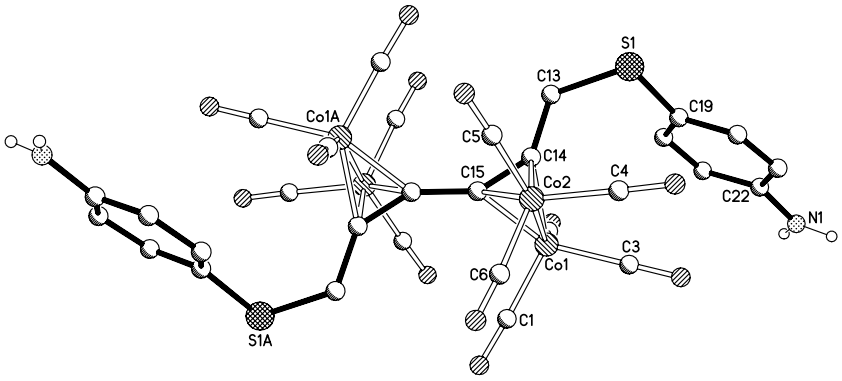


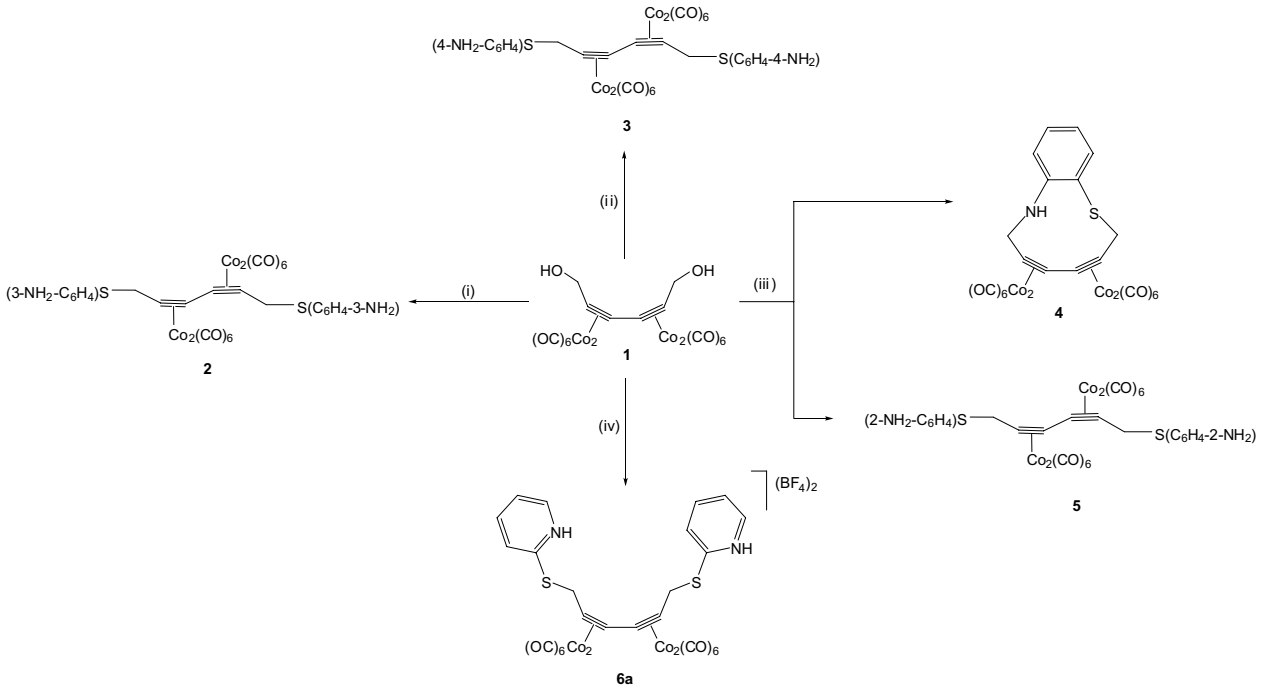
Fig. 2b. Molecular structure of **3** (molecule B: *trans*-aryls) with partial atom labeling scheme; all hydrogen atoms apart from the amino hydrogens, have been omitted for clarity.

CH_2S (C_6H_4-4-NH_2) chain in which the alkynic moieties are each coordinated by a $Co_2(CO)_6$ unit in an η^2:η^2 fashion with the relative disposition of aryl groups defining the isomeric description (*viz*. *cis*/*trans* aryls). The Co_2C_2 cores adopt the expected tetrahedral arrangements with the Co–Co and C(alkyne)–C(alkyne) bond distances falling within the normal ranges [15–17]. The two Co_2C_2 units in each isomer are disposed mutually *trans* [tors.: C(14)–C(15)–C(16)–C(17) 180.0° (molecule A) C(14)–C(15)–C(15A)–C(14A) 180.0°; (molecule B)], a configuration that is observed in the majority of crystallographically characterised neutral acyclic 1,3-diyne complexes [16]; complex **1** being an exception [14c]. The C≡C–CH_2 *bend-back* angles [C(13)–C(14)–C(15) 140.8(8)°, C(18)–C(17)–C(16) 140.8 (8)° (molecule A); C(13)–C(14)–C(15) 138.8(2)° (molecule B)] are slightly lower than those found in related acyclic cobalt–alkyne complexes; the mean C≡C–CH_2 angle is 141.31° [18]. Some evidence for delocalisation is apparent in the C(15)–C(16) [1.407(11) Å] and C(15)–C(15A) [1.424(16) Å] bonds of both molecules, a feature that has also been observed in other bis($Co_2(CO)_6$)-coordinated 1,3-diyne complexes [16,17]. Each cobalt atom is coordinated by three carbonyl ligands which display the expected linear geometries. Some differences are apparent at the propargylic carbon atoms between isomers with the C(14)–C(13)–S(1) angle in molecule A being notably

Table 2
Selected bond distances (Å) and angles (°) for **3**

Molecule A		Molecule B	
Bond lengths			
C(22)–N(1)	1.400(13)	C(22)–N(1)	1.402(14)
C(19)–S(1)	1.781(1)	C(19)–S(1)	1.766(9)
C(13)–S(1)	1.819(9)	C(13)–S(1)	1.811(9)
C(13)–C(14)	1.470(12)	C(13)–C(14)	1.501(13)
C(14)–C(15)	1.362(12)	C(14)–C(15)	1.346(12)
Co(1)–Co(2)	2.4781(16)	Co(1)–Co(2)	2.4706(18)
Co–C (carbonyl)	1.785(10)–1.860(12)	Co–C (carbonyl)	1.794(12)–1.842(11)
C–O (carbonyl)	1.114(12)–1.136(11)	C–O (carbonyl)	1.103(13)–1.156(13)
Co–C (alkyne)	1.950(8)–1.978(7)	Co–C (alkyne)	1.944(9)–1.972(9)
C(15)–C(16)	1.407(11)	C(15)–C(15A)	1.424(16)
C(16)–C(17)	1.357(12)		
C(17)–C(18)	1.482(12)		
C(18)–S(2)	1.807(9)		
S(2)–C(25)	1.770(9)		
C(28)–N(2)	1.399(14)		
Co(3)–Co(4)	2.4788(16)		
Bond angles			
C(19)–S(1)–C(13)	103.5(4)	C(19)–S(1)–C(13)	105.0(4)
S(1)–C(13)–C(14)	113.3(6)	S(1)–C(13)–C(14)	117.0(6)
C(13)–C(14)–C(15)	140.8(8)	C(13)–C(14)–C(15)	138.8(8)
C(14)–C(15)–C(16)	143.7(8)	C(14)–C(15)–C(15A)	146.2(11)
C(15)–C(16)–C(17)	147.0(8)		
C(16)–C(17)–C(18)	140.0(8)		
C(17)–C(18)–S(2)	117.0(6)		
C(18)–S(2)–C(25)	104.9(4)		

Atoms with suffix A are generated by symmetry ($1-x+1$, $-y+1$, $-z+2$).



Scheme 1. Reagents and conditions: (i) 3-$NH_2C_6H_4SH$, xs. $HBF_4 \cdot OEt_2$, −78 °C, CH_2Cl_2; (ii) 4-$NH_2C_6H_4SH$, xs. $HBF_4.OEt_2$, −78 °C, CH_2Cl_2; (iii) 2-$NH_2C_6H_4SH$, xs. $HBF_4.OEt_2$, −78 °C, CH_2Cl_2; (iv) 2-HSC_5H_4N, $HBF_4.OEt_2$, −78 °C, CH_2Cl_2.

smaller [113.3(6)°] than the corresponding angle [117.0(6)°] in the molecule B. Inspection of the packing picture reveals no significant intermolecular contacts.

The IR spectra of **2** and **3** are almost identical, with four bands in the *v*(CO) region in a pattern similar to that seen in related non-cyclic bis(dicobalt hexacarbonyl)-coordinated diyne complexes [15,16]. The LSI mass spectra display fragmentation peaks corresponding to the loss of carbonyl groups from the proposed molecular ions while the electrospray mass spectrum of **2** shows a peak for the protonated form of the molecular ion. The ^1H and ^{13}C NMR spectra give the expected distribution of signals with the equivalent propargyl carbon atoms and the proparylic hydrogens in **2** and **3** seen as singlets in both the ^{13}C NMR and ^1H NMR spectra, respectively.

Reaction of **1** with slightly greater than 2 equiv of 2-aminothiophenol in the presence of an excess of $HBF_4 \cdot OEt_2$ in dichloromethane at −78 °C gave [{$Co_2(CO)_6$}$_2${*cyclo*-μ-η^2:μ- η^2- $CH_2C_2C_2CH_2SC_6H_3$–NH-2}] (**4**) and [{$Co_2(CO)_6$-(μ-η^2-(2-NH_2–C_6H_4S)$CH_2C{\equiv}C$–)}$_2$] (**5**) in a 7:10 ratio (Scheme 1). Complex **5** could be formed as the unique product when a large excess of 2-aminothiophenol was employed. Complexes **4** and **5** have been characterised by LSI mass spectrometry and by ^1H and ^{13}C NMR and IR spectroscopy (see Table 1 and Section 4). In addition, both complexes have been the subject of single crystal X-ray diffraction studies.

Crystals of complex **4** and **5** suitable for the single crystal X-ray diffraction studies were grown from dichloromethane at 0 °C by slow diffusion of hexane. The molecular structure of **4** is shown in Fig. 3; selected bond lengths and angles are collected in Table 3. The structure consists of a 10-membered S–C–C≡C–C≡C–C–N–C═C– ring in which the two alkyne moieties are perpendicularly bound by two $Co_2(CO)_6$ units. The bond parameters within the Co_2C_2 cores fall in the normal ranges [15–17] with the relative disposition of the cores being best described as pseudo *cis* [tors. C(14)–C(15)–C(16)–C(17) 42.7°]. The *bend-back* angles are inequivalent with the C(13)–C(14)–C(15)

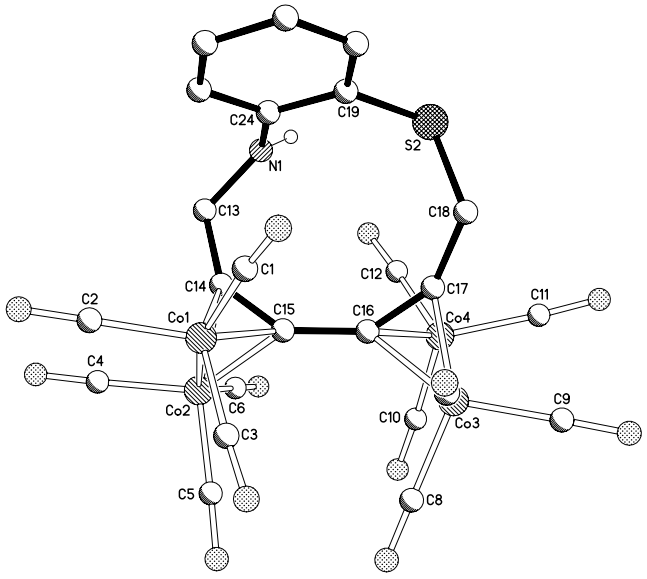


Fig. 3. Molecular structure of **4** with partial atom labeling scheme; all hydrogen atoms have been omitted for clarity.

Table 3
Selected bond distances and angles for **4**

Bond lengths (Å)			
N(1)–C(13)	1.455(4)	C(19)–C(24)	1.411(4)
C(13)–C(14)	1.501(4)	C(24)–N(1)	1.387(4)
C(14)–C(15)	1.351(3)	Co(1)–Co(2)	2.4647(6)
C(15)–C(16)	1.436(4)	Co(3)–Co(4)	2.4630(6)
C(16)–C(17)	1.355(4)	Co–C (carbonyl)	1.786(3)–1.839(3)
C(17)–C(18)	1.481(4)	C–O (carbonyl)	1.122(4)–1.137(4)
C(18)–S(2)	1.834(3)	Co–C (alkyne)	1.953(3)–1.990(3)
S(2)–C(19)	1.778(3)		
Bond angles (°)			
N(1)–C(13)–C(14)	113.0(2)	C(17)–C(18)–S(2)	115.4(2)
C(13)–C(14)–C(15)	140.1(3)	C(18)–S(2)–C(19)	101.56(14)
C(14)–C(15)–C(16)	142.5(3)	S(2)–C(19)–C(24)	120.3(3)
C(15)–C(16)–C(17)	143.1(3)	C(19)–C(24)–N(1)	120.3(3)
C(16)–C(17)–C(18)	145.7(3)		

angle being significantly less (by 5.6°) than the C(16)–C(17)–C(18) angle. It is tempting to ascribe this difference to the presence of the nitrogen and sulfur atoms that are linked to C(13) and C(18), respectively. However, inspection of the corresponding angles in the related complex [{$Co_2(CO)_6$}$_2$(μ-η^2:μ-η^2-*cyclo*-1,2-S–C_6H_4–$SCH_2C{\equiv}CC$-CCH_2)], in which the N(1) atom in **4** is replaced by a sulfur atom, reveals a similar asymmetry, albeit less significant (3.6° variation) [10]. The torsion angles of 67.8° and 94.1° for C(24)–N(1)–C(13)–C(14) and C(19)–S(2)–C(18)–C(17) indicate significant deviations from the preferred *gauche* arrangements [19] of C–E–C–C (E = heteroatom) bonds which is likely enforced by the rigid 1,2-C_6H_4 linker. No significant intermolecular interactions are apparent.

The molecular structure of **5** is shown in Fig. 4; selected bond lengths and angles are presented in Table 4. The molecular structure contains a crystallographic centre of symmetry which lies at the midpoint of the C(7)–C(7A) bond. The structure of **5** resembles **3** (molecule B: *trans*-aryls) with a bis($Co_2(CO)_6$)-coordinated hexa-2,4-diyne chain in this case end-capped by two S(2-NH_2–C_6H_4) groups. As with both isomers of **3**, the Co_2C_2 cores in **5** are also configured in a *trans*-disposition [tors: C(8)–C(7)–C(7A)–C(8A) 180°]. The geometric features within each Co_2C_2 core are unexceptional while the *bend-back* angle [C(9)–C(8)–C(7) 136.4(3)°] is lower than in **3**.

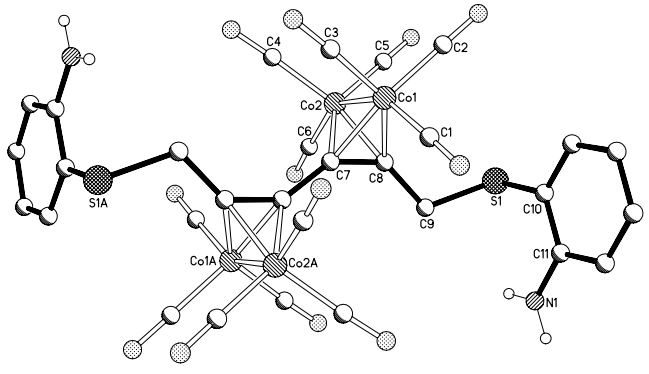


Fig. 4. Molecular structure of **5** with partial atom labeling scheme; all hydrogen atoms have been omitted for clarity.

The pattern of terminal carbonyl bands in IR spectra of **4** and **5** is similar to that seen for **2** and **3** and indeed is typical of other bis(dicobalt hexacarbonyl)-coordinated diyne complexes [15,16]. In the ^{1}H NMR spectrum of **4**, there are two propargyl CH_2 signals at δ 5.00 (CH_2NH) and 4.27 (CH_2S) whereas in **5** the equivalent CH_2 signals are seen as singlet at δ 4.29. Furthermore, the NH–CH_2 connectivity in **4** is confirmed by a three-bond coupling ($^3J_{HH}$ 7 Hz) between the corresponding protons. The ^{13}C NMR spectra supports the unsymmetrical nature of complex **4** with four alkynic carbon signals (δ 101.6, 97.2, 93.8 and 92.8) and two methylene carbon signals (δ 49.3, 45.3). Molecular ion peaks in the LSI mass spectra are seen for both **4** and **5** along with fragmentation peaks corresponding to the loss of carbonyl groups.

Higher yields of **4** could be achieved by treating **1** with firstly $HBF_4 \cdot OEt_2$ to generate the dication [{$Co_2(CO)_6$}$_2$ {μ-η^2:μ-η^2-($CH_2C{\equiv}C)_2$}][BF_4]$_2$ [14c,20] and then with 2-aminothiophenol to afford **4** as the sole product. It would therefore seem likely that the protic media involved in these Nicholas-type reactions inhibits N-alkylation of the primary amine in 2-aminothiophenol (or an intermediate). Indeed, it has been previously suggested that the propargy-

Table 4
Selected bond distances and angles for **5**

Bond lengths (Å)			
C(10)–S(1)	1.774(3)	Co(1)–Co(2)	2.4704(5)
C(9)–S(1)	1.823(3)	Co–C (carbonyl)	1.784(3)–1.831(4)
C(9)–C(8)	1.487(4)	C–O (carbonyl)	1.126(5)–1.135(5)
C(8)–C(7)	1.348(4)	Co–C (alkyne)	1.947(3)–1.977(3)
C(7)–C(7A)	1.434(6)		
Bond angles (°)			
C(10)–S(1)–C(9)	101.93(15)	C(9)–C(8)–C(7)	136.4(3)
S(1)–C(9)–C(8)	115.8(3)	C(8)–C(7)–C(7A)	143.8(3)

Atoms with suffix A are generated by symmetry ($1-x+2$, $-y+1$, $-z$).

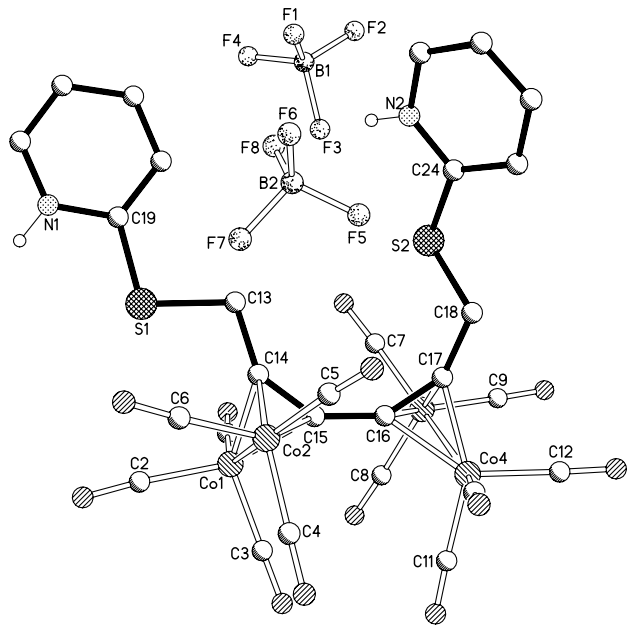


Fig. 5. Molecular structure of **6a** with partial atom labeling scheme; all hydrogen atoms apart from H1 and H2, have been omitted for clarity.

lation of polyfunctional primary and secondary amines with $[Co_2(CO)_6\{\mu\text{-}\eta^2\text{-}HC{\equiv}CCH_2\}](BF_4)$ in protic media should not proceed as the amino groups would be rendered inactive due to their complete protonation [13a]. Notably in this particular reaction, cyclic **4** could also be obtained (in addition to **5**) when the reaction is performed in the presence of a large excess of $HBF_4 \cdot OEt_2$; albeit in lower yield.

Given the observed importance of the 1,2-substitution pattern of amino/thiohydroxy groups in the above aromatics on macrocyclic formation, we decided to explore the reaction of **1** with 2-mercaptopyridine. While the pyridine unit in 2-mercaptopyridine contains no deprotonatable hydrogen atoms (*cf.* amino groups in *x*-NH_2–C_6H_4SH), it was envisaged that a dual *S*,*N*-centred nucleophilic attack may result via $N_{pyridinium}$–$C_{propargylic}$ bond formation [14c,20]. Thus, reaction of **1** with 2-mercaptopyridine in the presence of excess $HBF_4 \cdot OEt$ was carried out. However, only the bis-capped products, $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}(2\text{-}S\text{-}C_5H_4NH)CH_2C{\equiv}C\text{–})\}_2](BF_4)_2$ (**6a**) or $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}(2\text{-}S\text{–}C_5H_4N)CH_2C{\equiv}C\text{–})\}_2]$ (**6b**) could be isolated in moderate to good yields (Scheme 1), the precise identity being dependent on the work-up employed (see Section 4). Both **6a** and **6b** have been characterised by LSI mass spectrometry and by ^1H and ^{13}C NMR and IR spectroscopy (see Table 1 and Section 4). In addition, **6a** has been the subject of a single crystal X-ray diffraction study.

Crystals of **6a** suitable for the single crystal X-ray diffraction studies were grown by prolonged standing in a mixture of tetrahydrofuran and hexane. A view of **6a** is shown in Fig. 5; selected bond lengths and angles are presented in Table 5. The molecular structure consists of a dicationic complex and two tetrafluoroborate anions along with two lattice molecules of THF. The dication is based on a doubly SR-capped hexa-2,4-diyne chain where the R groups are pyridinium. Unlike in the straight chain complexes **3** and **5**, the Co_2C_2 cores in **6a** are *cis* to one another [tors. C(14)–C(15)–C(16)–C(17) 39.7°] in a manner similar to that seen in cyclic **4** and other cyclic 1,3-diyne complexes [10–12,21]. In the case of **6a**, the *cis*-configuration is probably stabilised by hydrogen-bonding interactions of the N–H and C–H protons in neighbouring pyridinium groups with the fluorine atoms of the two BF_4^- anions that are found inside the "cavity" formed by the two pyridinium moieties [closest NH(2)···F contacts: 2.135 and 2.366 Å; closest CH···F contacts: 2.600, 2.653 Å]. The pyridinium N–H proton facing away from the BF_4 anions additionally undergoes a hydrogen bonding interaction [NH(1)···O (THF) 1.804 Å] with a lattice THF molecule.

The ^1H and ^{13}C NMR spectra of **6a** and **6b** show only minor changes in chemical shift with a slight downfield influence on the signals evident in cationic **6a**. The pyridinium N–H protons in **6a** are visible as a broad downfield singlet at δ 11.0. In the LSI mass spectrum of **6a**, peaks corresponding to loss of BF_4 ions and CO groups from the proposed molecular ion are evident. A similar carbonyl fragmentation pattern was observed in the mass spectrum

Table 5
Selected bond distances and angles for **6a**

Bond lengths (Å)			
C(19)–S(1)	1.734(4)	Co(1)–Co(2)	2.4512(6)
C(13)–S(1)	1.814(3)	Co(3)–Co(4)	2.4709(7)
C(13)–C(14)	1.491(5)	C(24)–S(2)	1.744(4)
C(14)–C(15)	1.354(5)	Co–C (carbonyl)	1.793(4)–1.826(5)
C(15)–C(16)	1.440(5)	C–O (carbonyl)	1.129(4)–1.139(5)
C(16)–C(17)	1.348(4)	Co–C (alkyne)	1.939(3)–1.967(3)
C(17)–C(18)	1.488(5)	B–F	1.323(6)–1.388(5)
C(18)–S(2)	1.816(3)		
Bond angles (°)			
C(19)–S(1)–C(13)	104.09(17)	C(15)–C(16)–C(17)	141.5(3)
S(1)–C(13)–C(14)	106.4(2)	C(16)–C(17)–C(18)	140.5(3)
C(13)–C(14)–C(15)	140.9(3)	C(17)–C(18)–S(2)	108.7(2)
C(14)–C(15)–C(16)	142.6(3)	C(18)–S(2)–C(24)	101.07(16)

Table 6
Crystallographic and data processing parameters for **3**–**5** and **6a**

Complex	**3**	**4**	**5**	**6a**
Formula	$C_{30}H_{16}Co_4N_2O_{12}S_2$	$C_{24}H_9Co_4NO_{12}S$	$C_{30}H_{16}Co_4N_2O_{12}S_2$	$C_{28}H_{14}B_2Co_4F_8N_2O_{12}S_2 \cdot 2C_4H_8O$
M	896.29	771.10	896.29	1188.08
Crystal size (mm^3)	$0.23 \times 0.18 \times 0.01$	$0.23 \times 0.23 \times 0.18$	$0.28 \times 0.23 \times 0.12$	$0.23 \times 0.05 \times 0.02$
Temperature (K)	180(2)	180(2)	180(2)	180(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$C2/c$	$Pbca$	$P\bar{1}$
a (Å)	10.2269(4)	32.5768(8)	17.6760(5)	8.9647(3)
b (Å)	15.8376(7)	11.4520(5)	8.3367(2)	16.3448(7)
c (Å)	16.3202(8)	16.1133(6)	23.4759(7)	16.9189(8)
α (°)	98.283(2)	90	90	72.988(2)
β (°)	102.252(2)	112.499(14)	90	78.426(2)
γ (°)	91.420(3)	90	90	83.341(2)
U ($Å^3$)	2552.0(2)	5553.8(3)	3459.40(16)	2318.04(17)
Z	3	8	4	2
D_l ($Mg\ m^{-3}$)	1.750	1.844	1.721	1.702
$F(000)$	1338	3040	1784	1188
μ(Mo-Kα) (mm^{-1})	2.103	2.487	2.068	1.592
Reflections collected	15410	22279	12371	18033
Independent reflections	10328	6369	3036	8010
R_{int}	0.1101	0.0589	0.0549	0.0689
Restraints/parameters	0/676	0/379	0/226	0/613
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0816$ $wR_2 = 0.1914$	$R_1 = 0.0372$ $wR_2 = 0.0728$	$R_1 = 0.0343$ $wR_2 = 0.0776$	$R_1 = 0.0428$ $wR_2 = 0.0686$
All data	$R_1 = 0.1436$ $wR_2 = 0.2440$	$R_1 = 0.0730$ $wR_2 = 0.0829$	$R_1 = 0.0511$ $wR_2 = 0.0844$	$R_1 = 0.0957$ $wR_2 = 0.0869$
Goodness-of-fit on F^2 (all data)	1.015	0.977	1.049	1.029

Data in common: graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|, wR_2 = [\Sigma w(F^2_o - F^2_c)^2/\Sigma w(F^2_o)^2]^{1/2}, w^{-1} = [\sigma^2(F_o)^2 + (aP)^2], P = [\max(F^2_o, 0) + 2(F^2_c)]/3$, where a is a constant adjusted by the program; goodness of fit $= [\Sigma(F^2_o - F^2_c)2/(n-p)]^{1/2}$ where n is the number of reflections and p the number of parameters.

of **6b** in addition to a molecular ion peak and a weak peak due to a M^++Na ion. As with other complexes in this work the IR spectra of **6a** and **6b** are similar with four bands in the ν(CO) region.

3. Conclusions

The use of aminothiophenols to facilitate the ring closure of propargylic cations derived from **1** has been studied and it has been shown that only the 1,2-substitution pattern can deliver dual *N*,*S*-centered nucleophilic attack. The resultant 10-membered macrocyclic ring complex (**4**) has been fully characterised. Attempts to extend this reactivity to 2-mercaptopyridines gave only linear products (**6**).

4. Experimental

4.1. General procedures and materials

Unless otherwise stated all experiments were carried out under an atmosphere of dry, oxygen-free argon, using standard Schlenk line techniques and solvents freshly distilled from appropriate drying agent [22]. NMR spectra were recorded in $CDCl_3$ using a Bruker DRX-500 or a AM-400 spectrometer with TMS as an external standard for ^1H and ^{13}C spectra. ^1H–^1H COSY and HMQC NMR experiments were employed to obtain ^1H–^1H and ^1H–^{13}C correlated spectra [23]. Infrared spectra were, unless otherwise stated, recorded in dichloromethane solution in 0.5 mm NaCl solution cells, using a Perkin–Elmer 1710 Fourier Transform Spectrometer. LSI (Liquid Secondary Ion) mass spectra were recorded on a Micromass Autospec high resolution double focusing mass spectrometer at the EPSRC National Mass Spectrometry Service Centre at the University of Wales Swansea. Electrospray (ESI) mass spectra were recorded on a Micromass Quattro LC instrument at the University of Cambridge, Mass Spectrometry Services. Elemental analyses were performed at the University of Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 mesh ASTM). All products are listed in order of decreasing R_f. The reagents, 2-aminothiophenol, 3-aminothiophenol, 4-aminothiophenol, 2-mercaptopyridine and tetrafluoroboric acid (54 wt.% in diethyl ether) were obtained from Aldrich Chemical Co. and used without further purification. [{$Co_2(CO)_6$-(μ-η^2-$HOCH_2C{\equiv}C$–)}$_2$] (**1**) was prepared by the literature method [14].

4.2. Synthesis of [{$Co_2(CO)_6(\mu\text{-}\eta^2\text{-}(3\text{-}NH_2\text{–}C_6H_4S)\text{-}CH_2C{\equiv}C\text{–})\}_2$] (**2**)

To a stirred solution of **1** (1.390 g, 2.04 mmol) and 3-aminothiophenol (0.47 ml, 4.50 mmol, 2.2 equiv) in dichloromethane (200 ml) at −78 °C under argon was added 0.9 ml of 54% HBF_4 in diethyl ether. The reaction mixture was allowed to warm to 0 °C and an excess of $NaHCO_3$ added. Following filtration through a plug of Celite, the solid residue was washed several times with dichloromethane until the washings became colourless. The residue was then extracted with acetonitrile. Careful evaporation of the acetonitrile solution afforded brown-green crystalline **2** (0.980 g, 52%). Complex **2**: Anal. Calc. for $C_{30}H_{16}Co_4N_2O_{12}S_2$ (896.29): C, 40.17; H, 1.79; N, 3.12. Found: C, 40.20; H, 1.83; N, 2.90%. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 198.7 (CO), 147.0, 136.8 (C, C_6H_4), 129.9, 118.6, 114.9, 113.3 (CH, C_6H_4), 99.9, 92.0 (C≡C), 38.4 (CH_2). MS (ESI): m/z 897 $(M+H)^+$.

4.3. Synthesis of [{$Co_2(CO)_6(\mu\text{-}\eta^2\text{-}(4\text{-}NH_2\text{-}C_6H_4S)CH_2\text{-}C{\equiv}C\text{–})\}_2$] (**3**)

To a stirred solution of **1** (1.378 g, 2.02 mmol) and 4-aminothiophenol (0.629 g, 5.03 mmol, 2.5 equiv) in dichloromethane (200 ml) at −78 °C under argon was added 0.9 ml of 54% HBF_4 in diethyl ether. The reaction mixture was warmed to 0 °C and an excess of $NaHCO_3$ added. Following filtration through a plug of $MgSO_4$, the filtrate was concentrated and the residue adsorbed onto silica and then added to the top of a chromatography column. Elution with hexane:ethyl acetate (1:1) afforded dark brown-green crystalline **3** (1.47 g, 81%) as the sole product. Complex **3**: Anal. Calc. for $C_{30}H_{16}Co_4N_2O_{12}S_2$ (896.29): C, 40.17; H, 1.79; N, 3.12. Found: C, 40.27; H, 1.91; N, 2.96%. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 198.7 (CO), 146.1 (C, C_6H_4), 133.2 (CH, C_6H_4), 123.4 (C, C_6H_4), 115.7 (CH, C_6H_4), 100.3, 91.9 (C≡C), 41.6 (CH_2).

4.4. Synthesis of [{$Co_2(CO)_6\}_2${cyclo-$\mu\text{-}\eta^2$: $\mu\text{-}\eta^2$-$CH_2C_2C_2CH_2SC_6H_3$–NH-2}] (**4**) and [{$Co_2(CO)_6(\mu\text{-}\eta^2\text{-}(2\text{-}NH_2\text{–}C_6H_4S)CH_2C{\equiv}C\text{–})\}_2$] (**5**)

To a stirred solution of **1** (1.223 g, 1.79 mmol) and 2-aminothiophenol (0.493 g, 0.417 ml, 3.95 mmol, 2.2 equiv) in dichloromethane (400 ml) at −78 °C under argon was added 0.8 ml of 54% HBF_4 in diethyl ether. The resulting mixture was warmed to room temperature and an excess of $NaHCO_3$ added. Following filtration through a plug of $MgSO_4$, the filtrate was concentrated under reduced pressure. The residue was re-dissolved in the minimum amount of dichloromethane, adsorbed onto silica and added to the top of a chromatography column. Elution with hexane:ethyl acetate (6:1) afforded dark brown crystalline **4** (0.480 g, 35%). Further elution with hexane:ethyl acetate (4:1) yielded dark brown-green crystalline **5** (0.820 g, 51%). Complex **4**: Anal. Calc. for $C_{24}H_9Co_4NO_{12}S$ (771.10): C, 37.38; H, 1.17; N, 1.82. Found: C, 37.53; H, 1.37; N, 1.64%. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 199.8 (CO), 149.4 (C, C_6H_4), 138.3, 131.4 (CH, C_6H_4), 122.1 (C, C_6H_4), 120.6, 114.7 (CH, C_6H_4), 101.6, 97.2, 93.8, 92.8 (C≡C–C≡C), 49.3, 45.3 (CH_2). Complex **5**: Anal. Calc. for $C_{30}H_{16}Co_4N_2O_{12}S_2$ (896.29): C, 40.17; H, 1.79; N, 3.12. Found: C, 40.01; H, 1.96; N, 2.90%. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 199.7 (CO), 147.9 (C, C_6H_4), 135.2, 130.1, 118.7 (CH, C_6H_4), 117.7 (C, C_6H_4), 115.1 (CH, C_6H_4), 99.6, 91.6 (C≡C), 39.4 (CH_2).

4.5. Synthesis of [{$Co_2(CO)_6\}_2${cyclo-$\mu\text{-}\eta^2$:$\mu\text{-}\eta^2$-$CH_2C_2C_2CH_2SC_6H_3$–NH-2}] (**4**)

To a stirred solution of **1** (0.984 g, 1.44 mmol) in dichloromethane (400 ml) at −78 °C under argon was added 0.8 ml of 54% HBF_4 in diethyl ether. After 30 min at −78 °C, 2-aminothiophenol (0.155 ml, 1.44 mmol, 1 equiv) was added and the reaction mixture allowed to warm to room temperature and an excess of $NaHCO_3$ added. Following filtration through a plug of $MgSO_4$, the solvent removed under reduced pressure. The residue was re-dissolved in the minimum amount of dichloromethane, adsorbed onto silica and added to the top of a chromatography column. Elution with hexane:dichloromethane (4:1) afforded dark brown crystalline **4** (0.724 g, 65%) as the sole product.

4.6. Synthesis of [{$Co_2(CO)_6(\mu\text{-}\eta^2\text{-}(2\text{-}S\text{–}C_5H_4NH)CH_2\text{-}C{\equiv}C\text{–})\}_2$]$(BF_4)_2$ (**6a**)

To a stirred solution of **1** (0.700 g, 1.03 mmol) and 2-mercaptopyridine (0.250 g, 2.25 mmol, 2.2 equiv) in dichloromethane (200 ml) at −78 °C under argon was added 3.0 ml of 54% HBF_4 in diethyl ether. The resulting mixture was warmed to 0 °C and filtered through a plug of silica. The residue remaining on the plug was extracted with ethyl acetate and THF. The organic phases were combined and the solvent was removed on a rotary evaporator to give dark brown crystalline complex **6a** (1.200 g, 98%). Complex **6a**: Anal. Calc. for $C_{28}H_{14}Co_4N_2O_{12}S_2B_2F_8$ (1043.35): C, 32.20; H, 1.34; N, 2.68. Found: C, 32.36; H, 1.51; N, 2.52%. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 199.5 (CO), 157.5 (C, C_5H_4NH), 149.5, 136.9, 122.6, 120.3 (CH, C_5H_4NH), 103.7, 93.2 (C≡C), 34.1 (CH_2S).

4.7. Synthesis of [{$Co_2(CO)_6(\mu\text{-}\eta^2\text{-}(2\text{-}S\text{–}C_5H_4N)CH_2\text{-}C{\equiv}C\text{–})\}_2$] (**6b**)

To a stirred solution of **1** (0.450 g, 6.6 mmol) and 2-mercaptopyridine (0.895 g, 8.1 mmol, 1.2 equiv) in dichloromethane (500 ml) at −78 °C under argon was added 3.0 ml of 54% HBF_4 in diethyl ether. The reaction mixture was warmed to 0 °C and stirred overnight before an excess of $NaHCO_3$ was added. Following filtration through a plug of silica, the solvent was removed under reduced pressure. Crystallisation of the residue from hexane:dichloromethane

afforded dark brown-green crystalline **6b** (0.234 g, 40%). Complex **6b**: $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 198.8 (CO), 157.2 (C, C_5H_4N), 149.2, 136.2, 122.4, 119.9 (CH, C_5H_4N), 102.6, 92.4 (C≡C), 34.0 (CH_2S). ^1H NMR COSY: 8.41–8.40 (7.00), 7.50–7.48 (7.2, 7.00), 7.21–7.20 (7.5, 7.00), 7.00 (7.5, 7.2). HMQC: 8.41–8.40 (149.2), 7.50–7.48 (136.2), 7.21–7.20 (122.4), 7.00 (119.9), 4.83 (34.0).

4.8. Crystallographic studies

Single crystal X-ray diffraction data for **3**–**5** and **6a** were collected using a Nonius-Kappa CCD diffractometer, equipped with an Oxford Cryosystems cryostream and employing Mo-Kα ($\lambda = 0.71073$ Å) irradiation from a sealed tube X-ray source. Cell refinement, data collection and data reduction were performed with the programs DENZO [24] and COLLECT [25] and multi-scan absorption corrections were applied to all intensity data with the program SORTAV [26]. All structures were solved and refined with the programs SHELXS97 and SHELXL97 [27], respectively. Hydrogen atoms were included in calculated positions (C–H = 0.96 Å) riding on the bonded atom with isotropic displacement parameters set to $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(C) for all other H atoms. Details of the data collection, refinement and crystal data are listed in Table 6.

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Appendix A. Supplementary material

CCDC 651125, 651124, 651126 and 651123 contain the supplementary crystallographic data for **3**, **4**, **5** and **6a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.07.015.

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