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ARTICLE TYPE

## Avoiding problem reactions at the ferrocenyl-alkyne motif: a convenient synthesis of model, redox-active complexes for molecular electronics

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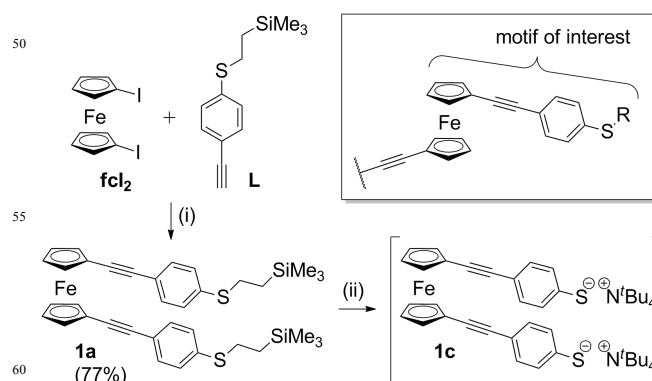
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A much improved route to 1,1'-bis(arylethynyl)ferrocenes comprising accessible thiolates on the aryl ring is reported. Unanticipated reactions between AcCl, TBAF/BBr<sub>3</sub> and ferrocenyl-alkynes are also discussed, offering a rationale for previous synthetic difficulties.

Metal-containing materials comprising surface-binding substituents are highly desirable for electron transfer studies,<sup>1</sup> yet their preparation is not always straightforward. Redox/coordination centres readily complicate routes normally trivial with all-organic analogues (via redox events or ligand association, dissociation, activation or deactivation), often resulting in poor yields or persistent, non-innocent impurities. These problems can delay and/or severely hinder investigations into entire classes of compounds that may exhibit a wide range of interesting electrochemical, photochemical and magnetic properties.<sup>1c,2</sup> In this communication we specifically address complications which have limited access to important model systems of the type  $\text{fc}(\text{C}\equiv\text{C}-\text{R})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{S}^-)$  (Scheme 1). Such complexes are in essence the ferrocene-containing equivalents of oligo(phenylene ethynylene)-type (OPE-type) molecular wires,<sup>3</sup> and are of particular importance given the ubiquity of gold-thiolate surface chemistry (commonly using  $-\text{SH}$  or  $-\text{SAc}$  functionalised precursors)<sup>4</sup> and the utility of ferrocene as a stable and accessible redox active component.<sup>5</sup>

The problem can be delineated as follows: (i) 1,1'-diethynylferrocene and 1-arylethynyl-1'-ethynylferrocenes appear unstable under conventional preparation conditions<sup>6</sup> and are not easily isolated/reacted *in situ*,<sup>7</sup> effectively stalling Sonogashira cross-coupling methodologies using 4-iodophenylthioacetate; (ii) cross-coupling of terminal alkynes and iodoferrocenes is impractical in the presence of thioacetyl moieties due to a competing coupling reaction<sup>8</sup> (though *aryl* iodides react without issue<sup>9</sup>); (iii) iodoferrocenes will cross-couple with the protected thiolate 1-(*tert*-butylsulfanyl)-4-ethynylbenzene, however difficulties have been encountered<sup>10</sup> in converting the *S*<sup>t</sup>Bu-terminus of relevant arylethynylferrocenes to  $-\text{SAc}$  (despite the success of this approach with other systems<sup>11</sup>); (iv) though it is possible to prepare  $\text{fc}(\text{C}\equiv\text{C}-\text{R})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{SAc})$ -type structures via Stille coupling from  $\text{fc}(\text{C}\equiv\text{C}-\text{R})(\text{C}\equiv\text{C}-\text{SnR}_3)$ ,<sup>12</sup> this requires additional steps and employs toxic reagents/intermediates.

As a result of these complications, despite the numerous examples reported,<sup>1g,10,12-13</sup> only a handful of thiolate/thioether-terminated 1,1'-bis(arylethynyl)ferrocene complexes may



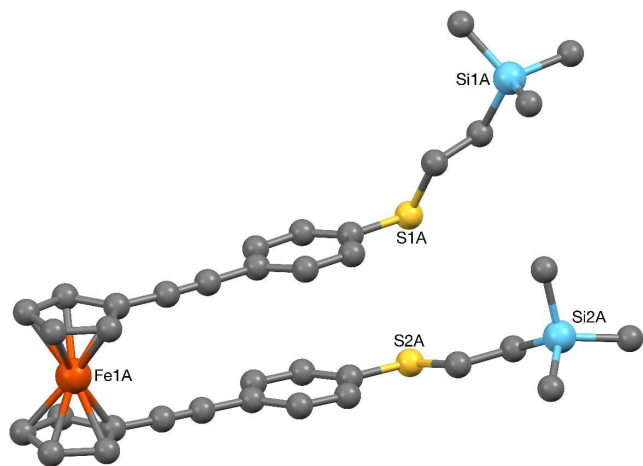
(i) Pd(P<sup>t</sup>Bu<sub>3</sub>)<sub>2</sub>, CuI, DIPA, THF; (ii) TBAF, THF

**Scheme 1** Synthesis of **1a** and **1c**. Top right: the structure-type which has (until now) proven difficult to prepare with readily cleavable R.

actually be utilized on surfaces as desired. It follows that electron transfer studies of such systems have so far only involved extended complexes,<sup>1b,1g</sup> with investigations concerning 'simple' (yet in no way less interesting) materials such as **1c** (Scheme 1) notable by their absence. We suggest that the aforementioned preparative issues have already had a marked impact on the wider research community.

The synthetic approach presented here was inspired by the work of Yu and Creager *et al.*,<sup>14</sup> who in 1999 reported successful Sonogashira cross-couplings of 1'-arylethynylferrocenes ( $\text{Fc}-[\text{C}\equiv\text{C}-\text{C}_6\text{H}_4]_n-\text{R}$ , where  $\text{R} = \text{I}$  or  $\text{C}\equiv\text{C}-\text{H}$ ) with arylthioethers comprising different thiolate protecting groups ( $\text{R}-[\text{C}\equiv\text{C}-\text{C}_6\text{H}_4]_n-\text{S}-\text{CH}_2\text{CH}_2-\text{R}^*$ , where  $\text{R} = \text{I}$  or  $\text{C}\equiv\text{C}-\text{H}$  and  $\text{R}^* = \text{C}_5\text{H}_5\text{N}$ ,  $\text{SiMe}_3$  or  $\text{SiMe}_2^t\text{Bu}$ ). Importantly, they demonstrated it was possible to remove the protecting groups in the presence of ferrocenyl-alkyne functionalities (forming  $-\text{S}^--\text{X}^+$ , where  $\text{X}^+ = \text{K}^+$  or  $\text{N}(\text{Bu})_4^+$ ), and subsequently studied the resulting complexes as monolayers on gold substrates. We resolved to determine whether these protecting groups might also prove stable during cross-couplings of iodoferrocenes (unlike  $-\text{SAc}$ <sup>8</sup>), and if 1,1'-bis(arylethynyl)ferrocenes might also survive the variety of synthetic transformations.

Our efforts started with the 2-(trimethylsilyl)ethyl functionality, given its apparent relatively facile incorporation and mild cleavage conditions. It has also been successfully utilised by others to protect thiolate-termini of additional (non-metallo) metal complexes.<sup>15</sup> Indeed, 2-(trimethylsilyl)ethyl-



**Fig. 1** The structure of one (**1a-A**) of the two independent molecules present in the crystal of **1a**.<sup>‡</sup>

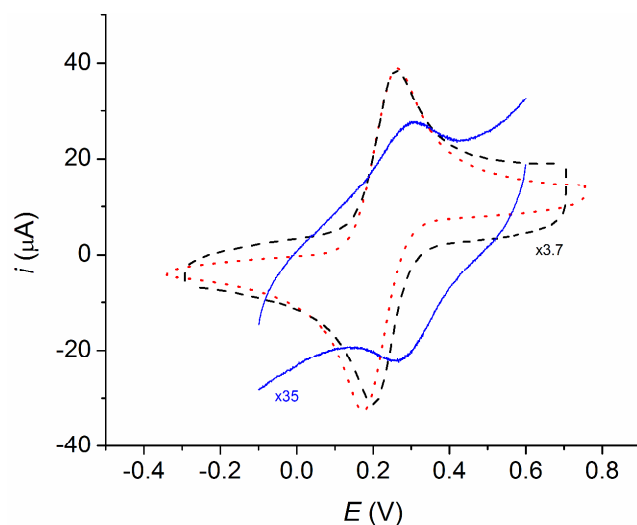
5 4<sup>+</sup>-(ethynyl)phenyl sulfide (**L**) was prepared without significant difficulty in four steps from commercially available 4-bromothiophenol (Scheme S-1).<sup>14a</sup> As an addendum to the literature procedure, we found that any residual starting material (**SM**) present after the first step is eliminated following onward reaction to, and workup of, 2-(trimethylsilyl)ethyl-4'-iodophenyl sulfide (**I-2**). Rather encouragingly, reaction of **L** with 1,1'-diiodoferrocene (**fcI<sub>2</sub>**) under Sonogashira cross-coupling conditions at room temperature<sup>8</sup> provided the intended product **1a** in 77% yield (Scheme 1). No evidence of protecting group

10 cleavage or competing cross-coupling reactions was observed. In addition to characterization by the usual techniques, this material was subjected to structural determination by X-ray crystallography (Fig. 1).<sup>‡</sup> More complex materials such as  $\text{fc}(\text{C}\equiv\text{C}-m\text{-Py})(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-S-CH}_2\text{CH}_2\text{-SiMe}_3)$  (**2**) and  $(\mu\text{-}3,5\text{-Py})(\text{C}\equiv\text{C}-[\text{fc}]\text{-C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-S-CH}_2\text{CH}_2\text{-SiMe}_3)_2$  (**3**) were also prepared using **L**, following our previously reported synthetic methodology for unsymmetrically substituted 1,1'-bis(arylethynyl)ferrocenes (Scheme S-2).<sup>10</sup>

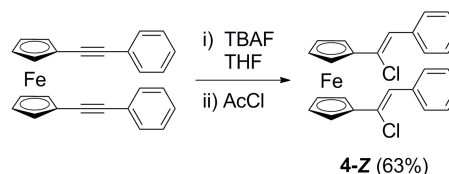
In testing the accessibility of the embedded sulfur-moieties we followed the trapping/surface electrochemistry strategies used by Yu and Creager *et al.*<sup>14</sup> Treatment of **1a** with tetra-*n*-butyl ammonium fluoride (TBAF) and quenching of the reaction mixture with MeI did indeed provide  $\text{fc}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{-SMe})_2$  (**1b**) in 77% yield (Scheme S-3). This result offers strong evidence for

15 *in situ* generation of the stable, intermediate thiolate species **1c** (Scheme 1). We also studied the surface electrochemistry of Au bead electrodes following their immersion in solutions of **1c** (**1c-Au**, for methodology see SI). Initial experiments in aqueous media using KClO<sub>4</sub> (sat. sol.), 0.1 M HClO<sub>4</sub> or 0.1 M KOH as electrolyte (with Pt counter and Ag/AgCl reference electrodes) proved difficult to interpret – under these conditions Au oxidation interfered with the redox chemistry of the layer (Fig. S-23). However, by changing reaction medium to CH<sub>3</sub>CN/0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (now using Pt counter and reference electrodes) a

20 reversible redox process typical of a surface confined species ( $\Delta E_p \sim 0$ ,  $I_p \propto \nu$ ,  $I_p^a/I_p^c \sim 1$ )<sup>1c</sup> was found at  $\Delta E_{1/2} = 0.28 \pm 0.01$  V vs. [FeCp<sub>2</sub>]<sup>+/</sup>[FeCp<sub>2</sub>]<sup>2+/</sup> (Fig. 2, blue solid line). The proximity of this equilibrium potential to those measured for **1a/1b** in CH<sub>2</sub>Cl<sub>2</sub>/0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> solution with a glassy carbon working



**Fig. 2** Solution (**1a**, black dashed line; **1b**, red dotted line) and surface (**1c-Au**, blue solid line) cyclic voltammograms (V vs. [FeCp<sub>2</sub>]<sup>+/</sup>[FeCp<sub>2</sub>]<sup>2+/</sup>,  $\nu = 0.1$  V/s, corrected for  $iR_s$ ).



**Scheme 2** Unexpected 'H-Cl' addition to  $\text{fc}(\text{C}\equiv\text{C}-\text{Ph})_2$  provided **4-Z** (Markovnikov product, *anti*-stereoselectivity). Product regio- and stereochemistry was deduced from 2D HMBC and ROESY NMR experiments (Fig. S-16 and S-17).

electrode ( $\Delta E_{1/2} \sim 0.23$  V, Table S-1) supports assignment of this redox process to surface-bound **1c** ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ). The relatively small difference in equilibrium potentials ( $\sim 0.05$  V) is ascribed to the changing molecular environments going from a solution phase to a surface-bound layer, and the electronic effects associated with thiolate deprotection/Au-coordination. Analogous surface electrochemical experiments using **1b** showed that the –SMe group also facilitates binding to gold surfaces ( $\Delta E_{1/2} = 0.31 \pm 0.01$  V vs. [FeCp<sub>2</sub>]<sup>+/</sup>[FeCp<sub>2</sub>]<sup>2+/</sup>).

Efforts to observe thiolate reduction peaks for **1c-Au** or **1b-Au**, and explore comparisons between them and the peaks assigned to  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , were hampered by the poly-crystallinity of the electrodes utilized in this study (peak broadening due to multiple Au–S environments), the high  $E_{1/2}$  of these materials in aqueous environments and the overlapping and intense solution-based redox events in acetonitrile (Fig. S-24). Though the nature of the molecule-surface interaction in **1b-Au** remains unclear, S–C bond cleavage has been known to occur under these conditions.<sup>16</sup> For additional details of electrochemical experiments with **1-4**, please see the supplementary information.

Given the success in transforming –SCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>3</sub> moieties to –SMe using TBAF/MeI, we considered the potential utility of acetyl chloride (AcCl) as a thiolate trapping agent (to provide –SAc). Interestingly however, attempts to convert the –SCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>3</sub> group of **1a** to –SAc (under otherwise identical

25 conditions to those used for **1b**) formed an initially puzzling

mixture of products in addition to the desired  $\text{fc}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-SAC})_2$  complex. Analogous experiments using 1,1'-bis(phenylethynyl)ferrocene as a control provided useful insights. We were surprised to observe the addition of 'H-Cl' across  $\text{C}\equiv\text{C}$ , resulting in the formation of  $\text{fc}(\text{C}(\text{Cl})=\text{C}(\text{H})-\text{C}_6\text{H}_5)_2$  (**4-Z**, Scheme 2) and associated isomers (note that it was only possible to isolate the former by conducting the reaction under specific conditions, see SI). Such ferrocenyl vinyl halides are more typically produced from reactions between acetylferrocenes and DMF/ $\text{POCl}_3$ ,<sup>17</sup> or through combinations of ethynylferrocenes and (i) aryl diazonium salts (Meerwein arylations) in acetone/5 M HCl,<sup>18</sup> or (ii)  $\text{SOCl}_2$ .<sup>19</sup> Additional control experiments reacting 1,1'-bis(phenylethynyl)ferrocene with AcCl or TBAF alone returned only starting material. Returning to our initial result from the reaction of **1a**, TBAF and AcCl, we were now able to identify some components of the mixture as  $\text{fc}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-SAC})(\text{C}_2\text{HCl}-p\text{-C}_6\text{H}_4\text{-SAC})$  and  $\text{fc}(\text{C}_2\text{HCl}-p\text{-C}_6\text{H}_4\text{-SAC})_2$  (Fig. S-18 and S-19).§

As discussed in the introduction, a common method to install -SAC functionalities is via the reaction of -S'Bu groups with  $\text{BBr}_3$  and AcCl<sup>11</sup> (though this has not previously proved successful with ferrocenyl-alkynes<sup>10</sup>). Given the reactions observed here between aryethynylferrocenes and TBAF/AcCl we were intrigued by the potential for related haloalkene-containing side products to form when using  $\text{BBr}_3/\text{AcCl}$ , and so subjected 1,1'-bis(phenylethynyl)ferrocene to the latter, under conditions typical for the conversion of Ar-S'Bu to Ar-SAC.<sup>10a,b</sup> From <sup>1</sup>H NMR spectroscopy and mass spectrometry, the formation of structurally similar chloroalkene-, and now also bromoalkene-functionalised products,  $\text{fc}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)(\text{C}_2\text{HX}-\text{C}_6\text{H}_5)$  and  $\text{fc}(\text{C}_2\text{HX}-\text{C}_6\text{H}_5)_2$  (X = Cl, Br) was indeed apparent (Fig. S-20 and S-21).§ This previously unrealised, enhanced reactivity of ferrocenyl-alkynes compared to aryl-alkynes clearly demonstrates why earlier attempts<sup>10</sup> to cleanly convert the -S'Bu moieties of such compounds to -SAC using the  $\text{BBr}_3/\text{AcCl}$  method<sup>11a,b</sup> were unsuccessful.

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## Conclusions

The 2-(trimethylsilyl)ethyl moiety functions as a remarkably effective protecting group for the construction of thiolate-substituted 1,1'-bis(arylethynyl)ferrocenes. Unlike -SAC, - $\text{SCH}_2\text{CH}_2\text{SiMe}_3$  termini are stable during Sonogashira couplings of iodoferrocenes and, in contrast to -S'Bu, are easily cleaved using TBAF to form robust, presumably ionic, species with a strong affinity for gold. By reducing design restrictions, it is hoped that this straightforward synthetic approach will facilitate broader surface studies comprising ferrocene-containing materials for molecular electronics, also providing new opportunities in sensing/molecule recognition and surface functionalization.<sup>4</sup> Given the potential for ferrocenyl-alkyne addition reactions in the presence of AcCl and TBAF/ $\text{BBr}_3$ , caution is advised in the choice of *tert*-butyl functionalities as thiolate protecting groups for any compounds containing electron rich alkynes. Through improving our understanding of the reactivity of the fascinating ferrocenyl-alkyne motif *in general*, we hope it can be better utilized in the future.

## Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures, NMR and mass spectra, electrochemical experiments and crystallographic information. See DOI: 10.1039/b000000x/

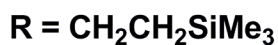
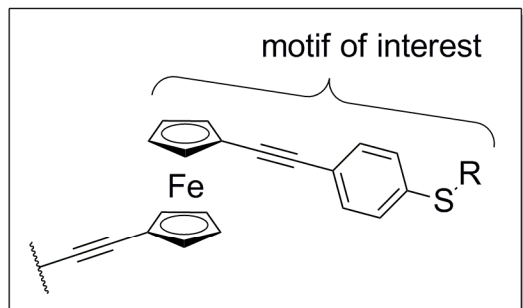
‡ Crystal data for **1a**:  $\text{C}_{36}\text{H}_{42}\text{FeS}_2\text{Si}_2$ ,  $M = 650.84$ , monoclinic,  $P2_1/n$  (no. 14),  $a = 26.4392(7)$ ,  $b = 9.4335(3)$ ,  $c = 30.5460(9)$  Å,  $\beta = 113.570(3)^\circ$ ,  $V = 6983.0(4)$  Å<sup>3</sup>,  $Z = 8$  (2 independent molecules),  $D_c = 1.238$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.643$  mm<sup>-1</sup>,  $T = 173$  K, orange platy needles, Agilent Xcalibur 3E diffractometer; 13764 independent measured reflections ( $R_{\text{int}} = 0.0248$ ),  $F^2$  refinement,<sup>[1]</sup>  $R_1(\text{obs}) = 0.0440$ ,  $wR_2(\text{all}) = 0.1076$ , 10060 independent observed absorption-corrected reflections [ $|F_o| > 4\sigma(|F_o|)$ ,  $2\theta_{\text{max}} = 56^\circ$ ], 790 parameters. CCDC 995891.

§ Regio- and stereochemical assignment of components in mixtures was impracticable due to overlapping resonances in their NMR spectra.  $\text{C}_2\text{HX} = \text{C}(\text{X})=\text{C}(\text{H})$  or  $\text{C}(\text{H})=\text{C}(\text{X})$ .

- (a) P. J. Low, *Dalton Trans.*, 2005, 2821; (b) S. A. Getty, C. Engtrakul, L. Wang, R. Liu, S.-H. Ke, H. U. Baranger, W. Yang, M. S. Fuhrer and L. R. Sita, *Phys. Rev. B*, 2005, **71**, 241401; (c) T. Albrecht, K. Moth-Poulsen, J. B. Christensen, A. Guckian, T. Bjørnholm, J. G. Vos and J. Ulstrup, *Faraday Discuss.*, 2006, **131**, 265; (d) A. K. Mahapatro, J. Ying, T. Ren and D. B. Janes, *Nano Lett.*, 2008, **8**, 2131; (e) A. L. Eckermann, D. J. Feld, J. A. Shaw and T. J. Meade, *Coord. Chem. Rev.*, 2010, **254**, 1769; (f) L. Luo, A. Benameur, P. Brignou, S. H. Choi, S. Rigaut and C. D. Frisbie, *J. Phys. Chem. C*, 2011, **115**, 19955; (g) C.-P. Chen, W.-R. Luo, C.-N. Chen, S.-M. Wu, S. Hsieh, C.-M. Chiang and T.-Y. Dong, *Langmuir*, 2013, **29**, 3106; (h) F. Lissel, T. Fox, O. Blacque, W. Polit, R. F. Winter, K. Venkatesan and H. Berke, *J. Am. Chem. Soc.*, 2013, **135**, 4051; (i) S. Marques-Gonzalez, D. S. Yufit, J. A. K. Howard, S. Martin, H. M. Osorio, V. M. Garcia-Suarez, R. J. Nichols, S. J. Higgins, P. Cea and P. J. Low, *Dalton Trans.*, 2013, **42**, 338.
- (a) F. Barigelletti and L. Flamigni, *Chem. Soc. Rev.*, 2000, **29**, 1; (b) J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruña, P. L. McEuen and D. C. Ralph, *Nature*, 2002, **417**, 722; (c) A. C. Benniston, *Chem. Soc. Rev.*, 2004, **33**, 573; (d) T. Albrecht, A. Guckian, J. Ulstrup and J. G. Vos, *Nano Lett.*, 2005, **5**, 1451.
- (a) J. M. Tour, L. Jones, D. L. Pearson, J. J. S. Lamba, T. P. Burgin, G. M. Whitesides, D. L. Allara, A. N. Parikh and S. Atre, *J. Am. Chem. Soc.*, 1995, **117**, 9529; (b) J. M. Tour, A. M. Rawlett, M. Kozaki, Y. X. Yao, R. C. Jagessar, S. M. Dirk, D. W. Price, M. A. Reed, C. W. Zhou, J. Chen, W. Y. Wang and I. Campbell, *Chem. Eur. J.*, 2001, **7**, 5118; (c) R. L. Carroll and C. B. Gorman, *Angew. Chem., Int. Ed.*, 2002, **41**, 4379; (d) K. Liu, G. Li, X. Wang and F. Wang, *J. Phys. Chem. C*, 2008, **112**, 4342; (e) V. Kaliginedi, P. Moreno-García, H. Valkenier, W. Hong, V. M. García-Suárez, P. Buitter, J. L. H. Otten, J. C. Hummelen, C. J. Lambert and T. Wandlowski, *J. Am. Chem. Soc.*, 2012, **134**, 5262.
- (a) J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.*, 2005, **105**, 1103; (b) C. Vericat, M. E. Vela, G. Benitez, P. Carro and R. C. Salvarezza, *Chem. Soc. Rev.*, 2010, **39**, 1805; (c) H. Hakkinen, *Nat. Chem.*, 2012, **4**, 443.
- (a) N. Chawdhury, N. J. Long, M. F. Mahon, L.-I. Ooi, P. R. Raithby, S. Rooke, A. J. P. White, D. J. Williams and M. Younus, *J.*

- Organomet. Chem.*, 2004, **689**, 840; (b) A. Hildebrandt and H. Lang, *Organometallics*, 2013, **32**, 5640.
6. J. K. Pudelski and M. R. Callstrom, *Organometallics*, 1992, **11**, 2757.
7. (a) H. Schottenberger, J. Lukasser, E. Reichel, A. G. Müller, G. Steiner, H. Kopacka, K. Wurst, K. H. Ongania and K. Kirchner, *J. Organomet. Chem.*, 2001, **637–639**, 558; (b) K. H. H. Fabian, H.-J. Lindner, N. Nimmerfroeh and K. Hafner, *Angew. Chem., Int. Ed.*, 2001, **40**, 3402; (c) M. I. Bruce, P. J. Low, F. Hartl, P. A. Humphrey, F. de Montigny, M. Jevric, C. Lapinte, G. J. Perkins, R. L. Roberts, B. W. Skelton and A. H. White, *Organometallics*, 2005, **24**, 5241; (d) J. Yoshino, R. Shimizu, N. Hayashi and H. Higuchi, *Bull. Chem. Soc. Jpn.*, 2011, **84**, 110; (e) G. Grelaud, G. Argouarch, M. P. Cifuentes, M. G. Humphrey and F. Paul, *Tetrahedron*, 2013, **69**, 3316.
8. M. S. Inkpen, A. J. P. White, T. Albrecht and N. J. Long, *Chem. Commun.*, 2013.
9. (a) D. L. Pearson and J. M. Tour, *J. Org. Chem.*, 1997, **62**, 1376; (b) C. Engtrakul and L. R. Sita, *Organometallics*, 2008, **27**, 927.
10. M. S. Inkpen, T. Albrecht and N. J. Long, *Organometallics*, 2013, **32**, 6053.
- 20 11. (a) N. Stuhr Hansen, *Synth. Commun.*, 2003, **33**, 641; (b) N. Stuhr-Hansen, J. K. Sørensen, K. Moth-Poulsen, J. B. Christensen, T. Bjørnholm and M. B. Nielsen, *Tetrahedron*, 2005, **61**, 12288; (c) J. B. Heilmann, E. A. Hillard, M.-A. Plamont, P. Pigeon, M. Bolte, G. Jaouen and A. Vessières, *J. Organomet. Chem.*, 2008, **693**, 1716.
- 25 12. (a) M. Vollmann and H. Butenschon, *C. R. Chim.*, 2005, **8**, 1282; (b) W.-W. Zhang, M. Kondo, T. Fujita, K. Namiki, M. Murata and H. Nishihara, *Molecules*, 2010, **15**, 150.
13. (a) C. Engtrakul and L. R. Sita, *Nano Lett.*, 2001, **1**, 541; (b) J. Ma, M. Vollmann, H. Menzel, S. Pohle and H. Butenschön, *J. Inorg. Organomet. Polym. Mater.*, 2008, **18**, 41; (c) I. Baumgardt and H. Butenschön, *Eur. J. Inorg. Chem.*, 2010, **2010**, 1076.
- 30 14. (a) C. J. Yu, Y. Chong, J. F. Kayyem and M. Gozin, *J. Org. Chem.*, 1999, **64**, 2070; (b) S. Creager, C. J. Yu, C. Bamdad, S. O'Connor, T. MacLean, E. Lam, Y. Chong, G. T. Olsen, J. Luo, M. Gozin and J. F. Kayyem, *J. Am. Chem. Soc.*, 1999, **121**, 1059.
- 35 15. (a) H.-M. Wen, D.-B. Zhang, L.-Y. Zhang, L.-X. Shi and Z.-N. Chen, *Eur. J. Inorg. Chem.*, 2011, **2011**, 1784; (b) A. Blum, T. Ren, D. A. Parish, S. A. Trammell, M. H. Moore, J. G. Kushmerick, G.-L. Xu, J. R. Deschamps, S. K. Pollack and R. Shashidhar, *J. Am. Chem. Soc.*, 2005, **127**, 10010.
- 40 16. (a) C.-J. Zhong and M. D. Porter, *J. Am. Chem. Soc.*, 1994, **116**, 11616; (b) T. Weidner, N. Ballav, M. Zharnikov, A. Priebe, N. J. Long, J. Maurer, R. Winter, A. Rothenberger, D. Fenske, D. Rother, C. Bruhn, H. Fink and U. Siemeling, *Chem. Eur. J.*, 2008, **14**, 4346.
- 45 17. (a) K. Schlögl and W. Steyrer, *Monatsh. Chem.*, 1965, **96**, 1520; (b) M. Rosenblum, N. Brawn, J. Papenmeier and M. Applebaum, *J. Organomet. Chem.*, 1966, **6**, 173; (c) M. Puciová, E. Solčániová, N. a. Pronayová, D. Loos and Š. Toma, *Tetrahedron*, 1993, **49**, 7733.
18. H. Nock and H. Schottenberger, *J. Org. Chem.*, 1993, **58**, 7045.
- 50 19. E. V. Banide, Y. Ortin, B. n. d. Chamiot, A. Cassidy, J. Niehaus, A. Moore, C. M. Seward, H. Müller-Bunz and M. J. McGlinchey, *Organometallics*, 2008, **27**, 4173.
20. SHELXTL, Bruker AXS, Madison, WI; SHELX-97, G.M. Sheldrick, *Acta Cryst.*, 2008, *A64*, 112-122; SHELX-2013, <http://shelx.uni-ac.gwdg.de/SHELX/index.php>
- 55

A much improved route to 1,1'-bis(arylethynyl)ferrocenes comprising *accessible* thiolates on the aryl ring is reported. Unanticipated reactions between AcCl, TBAF/BBr<sub>3</sub> and ferrocenyl-alkynes are also discussed, offering a rationale for previous synthetic difficulties.



stable under coupling conditions

readily cleaved with TBAF

