Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

UNSYMMETRICALLY DISUBSTITUTED FERROCENES
X*. SYNTHESIS OF 2,2″- AND 2,5″-DISUBSTITUTED BIFERROCENES BY THE DIRECT COUPLING OF 2-SUBSTITUTED LITHIOFERROCENES

D. J. BOOTH, G. MARR AND B. W. ROCKETT
Department of Physical Sciences, The Polytechnic, Wolverhampton, WV1 1LY (Great Britain)

(Received April 28th, 1971)

SUMMARY

A convenient and specific synthesis of 2,2″- and 2,5″-disubstituted biferrocenes by the coupling of 2-substituted lithioferrocenes in the presence of cobalt chloride is reported. Biferrocenes with (dimethylamino)methyl, 2-pyridyl and 2-quinolyl groups have been prepared from the corresponding monosubstituted ferrocenes.

In previous papers[1] we have described a synthetic route to specifically disubstituted biferrocenes through 2-[(dimethylamino)methyl]ferroceneboronic acid (III)[2]. The boronic acid (III) was prepared from [(dimethylamino)methyl]ferrocene (Ia) by metallation to give the lithio intermediate (IIa)[3] and condensation with tri-n-butyl borate, (see Scheme 1). These biferrocenes were characterized as diastereoisomers[1] with the substituents on carbon atoms 2 and 2″ (V) or 2 and 5″ (IV). The stereochemistry of these compounds has been investigated recently[4] and the unsymmetrical isomer (V) has been resolved into the enantiomers[4].

Previously the biferrocenes have not been readily accessible by substitution of the parent compound since the groups enter ring positions remote from the bond between the metallocene nuclei[5]. These reactions also led to mixtures of mono- and poly-substituted products when problems of separation and identification assume importance[5].

The direct coupling of lithioferrocene in the presence of anhydrous metal halides has been examined as a route to biferrocene[6]. However a mixture of bi-, ter- and higher poly-ferrocenes was obtained presumably through the presence of both mono- and di-lithioferrocene in the reaction mixture. Our utilization of specifically 2-substituted lithioferrocenes (II) in synthesis[3,7] indicated that these intermediates might be coupled to afford specifically disubstituted biferrocenes. Recently, the specific coupling of lithiated diarylmethanes to the corresponding symmetrical tetraarylmethanes by methylsulphonyl chloride[8] and substituted vinyllithium compounds to substituted butadienes by anhydrous cobalt chloride[9] have been reported.

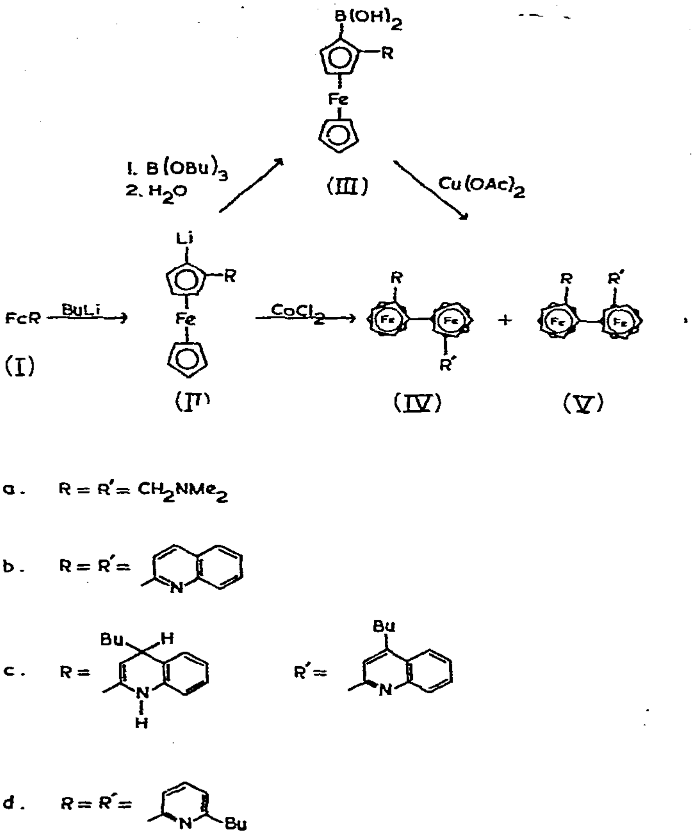
The lithioamine (IIa) prepared from the amine (Ia) was coupled in the presence of anhydrous cobalt chloride to give the biferrocenes [(IVa) and (Va)].

We have also prepared the quinolylbiferrocenes [(IVb) and (Vb)], the unsym-

---

* Part IX, see ref. 11.

SCHEME 1



metrical (butylquinolyl)biferrocenes [(IVc) and (Vc)] and the (butylpyridyl)biferrocenes [(IVd) and (Vd)] by this route. The reactions are summarized in the scheme. The isomeric biferrocenes [(IVa) and (Va)] were obtained in a total yield of 85%. This compares with an overall yield of 46% by the boronic acid route. The three isomeric pairs of biferrocenes [(IVb)–(IVd); (Vb)–(Vd)] with large substituent groups adjacent to the bond between the metallocene nuclei were formed in good yield by coupling of the appropriate lithioamines. This indicates that steric effects will be unimportant in the coupling reaction.

The isomeric biferrocenyls [(IV) and (V)] were separated in each case by chromatography on alumina. The product eluted first from the column invariably had the higher melting point and was presumably the symmetrical 2,5''-disubstituted isomer (IV) by analogy with the recent unambiguous assignment of structure[4]. The second biferrocene to be eluted was presumably the unsymmetrical 2,2''-disubstituted compound (V).

The diferrocenes [(IVa)–(IVc) and (Va)–(Vc)] were characterized by elemental analysis and infrared spectroscopy. The principal infrared absorption frequencies are listed in the Experimental section.

EXPERIMENTAL

For general directions see Part I[7a].

2,2''- *And 2,5''-bis[(dimethylamino)methyl]biferrocene, (Va) and (IVa)*

[(Dimethylamino)methyl]ferrocene (4.86 g, 0.02 mole) was dissolved in dry ether (100 ml) and n-butyllithium (0.03 mole) in hexane was added. After stirring for 15 min at room temperature the solution was cooled to −78° and anhydrous cobalt(II) chloride (4.0 g, 0.031 mole) was added. The reaction mixture was allowed to warm slowly to room temperature and was stirred for 1 h. The mixture was quenched by the cautious addition of water and was made basic with an excess of 1 *M* sodium hydroxide. The black suspension was extracted with several portions of benzene and the extracts dried ($MgSO_4$), evaporated to low bulk and chromatographed on alumina in benzene/light petroleum. Ether/light petroleum mixtures eluted the 2,5''-biferrocene (IVa) (1.8 g, 61%*), identified by comparison with an authentic sample. Ether eluted the starting material (Ia) (1.9 g). Methanol/ether eluted the 2,2''-biferrocene (Va) (0.7 g, 24%) identified by comparison with an authentic sample.

2,2''- *And 2,5''-bis[2-(6-butylpyridyl)]biferrocene, (Vd) and (IVd)*

The reaction between 2-butyl-6-ferrocenylpyridine (1.77 g, 0.0055 mole) purified by GLC on a 7' × $\frac{3}{8}$'' column of 20% methyl silicone gum (E 30) on celite in dry ether (100 ml), n-butyllithium (0.017 mole) in hexane (10.5 ml) and anhydrous cobalt(II) chloride (4.0 g, 0.031 mole) was carried out as described above and the product was chromatographed on alumina in benzene/light petroleum. Benzene/light petroleum eluted the starting material (0.464 g, 26%). Benzene eluted 2,5''-bis[2-(6-butylpyridyl)]biferrocene (IVd) (0.346 g, 20%) which crystallized from light petroleum as dark orange granules, m.p. 108–109°. (Found: C, 71.55; H, 6.3; mol.wt. (vapour pressure of benzene), 629. $C_{38}H_{40}Fe_2N_2$ calcd.: C, 71.7; H, 6.35%; mol.wt., 636). Principal IR absorption frequencies 1587, 1574, 1479, 1109, 1009, 820, 817, 757 cm^{-1}. Benzene next eluted 2,2''-bis[2-(6-butylpyridyl)]biferrocene (Vd) (0.30 g, 17%) which crystallized from light petroleum as fine orange needles, m.p. 48–51°. (Found: C, 71.85; H, 6.4; mol.wt. (vapour pressure of benzene), 606. $C_{38}H_{40}Fe_2N_2$ calcd.: C, 71.7; H, 6.35%; mol.wt., 636). Principal IR absorption frequencies 1589, 1573, 1479, 1104, 1003, 813, 746 cm^{-1}.

2,2''- *And 2,5''-bis(2-quinolyl)biferrocene, (Vb) and (IVb)*

The reaction between (2-quinolyl)ferrocene (5.0 g, 0.016 mole) in dry ether (250 ml), n-butyllithium (0.047 mole) in hexane (30 ml) and anhydrous cobalt(II) chloride (10.0 g, 0.079 mole) was carried out as described above and the product was chromatographed on alumina in benzene/light petroleum. Benzene/light petroleum eluted 2-ferrocenyl-4-butyl-1,4-dihydroquinoline (0.192 g, 3.2%). Benzene eluted the starting material (1.715 g, 34%). Benzene next eluted 2,5''-bis(2-quinolyl)biferrocene (IVb) (0.280 g, 5.6%) which crystallized from light petroleum as fine orange granules, m.p. 247–248°. (Found: C, 73.2; H, 4.6; mol.wt. (vapour pressure of benzene), 655. $C_{38}H_{28}Fe_2N_2$ calcd.: C, 73.15; H, 4.5%; mol.wt., 624.) Principal IR absorption

---

* Yields are based on unrecovered starting material.

frequencies 1599, 1508, 1103, 1001, 823, 755 cm^{-1}. Benzene next eluted 2,2″-bis(2-quinolyl)biferrocene (Vb) (0.918 g, 18%) which crystallized as orange granules from benzene/light petroleum, m.p. 208–211°. (Found: C, 74.3; H, 4.65; mol.wt. (mass spectrum), 624. $C_{38}H_{28}Fe_2N_2$ calcd.: C, 73.15; H, 4.5%; mol.wt., 624.) Principal IR absorption frequencies 1599, 1509, 1102, 999, 823, 749, 675 cm^{-1}.

2,2″- *And* 2,5″-*disubstituted biferrocenes of* 4-*butyl*-1,4-*dihydroquinoline*, (*Vc*) *and* (*IVc*)

The reaction between 2-ferrocenyl-4-butyl-1,4-dihydroquinoline[10] (2.0 g, 0.0054 mole) in dry ether (100 ml), n-butyllithium (0.019 mole) in benzene (8 ml) and anhydrous cobalt(II) chloride (5.0 g, 0.039 mole) was carried out as described above and the product was chromatographed on alumina in benzene/light petroleum. Benzene/light petroleum eluted the starting material (0.660 g, 33%). Benzene/light petroleum eluted the 2,5″-biferrocene (IVc) (0.231 g, 12%) which precipitated from light petroleum as an orange powder m.p. 187–189° (dec.). (Found: C, 74.8; H, 6.1; mol.wt. (mass spectrum), 738. $C_{46}H_{46}Fe_2N_2$ calcd.: C, 74.8; H, 6.0%; mol.wt., 738.) Principal IR absorption frequencies 3350, 1601, 1489, 1473, 1110, 1010, 830, 820, 750 cm^{-1} Benzene/light petroleum next eluted the 2,2″-biferrocene (Vc) (0.206 g, 10%) which precipitated from light petroleum as an orange powder and which did not melt but decomposed from 110°. (Found: C, 74.7; H, 5.95; N, 3.7; mol.wt. (mass spectrum), 738. $C_{46}H_{46}Fe_2N_2$ calcd.: C, 74.8; H, 6.0; N, 3.8%; mol.wt., 738.) Principal IR absorption frequencies 3350, 1600, 1512, 1488, 1110, 1010, 835, 767, 750 cm^{-1}.

ACKNOWLEDGEMENTS

We wish to thank The Polytechnic, Wolverhampton for a research assistantship to D.J.B. and the Science Research Council for grants to purchase the preparative gas chromatography apparatus and for the hire of mass spectrometric facilities at the Physico-chemical Methods Unit, Harwell.

REFERENCES

1 G. Marr, R. E. Moore and B. W. Rockett, *Tetrahedron*, 25 (1969) 3477; G. Marr, R. E. Moore and B. W. Rockett, *Tetrahedron Lett.*, (1968) 2517.
2 G. Marr, R. E. Moore and B. W. Rockett, *J. Chem. Soc. C*, (1968) 24.
3 D. W. Slocum, B. W. Rockett and C. R. Hauser, *J. Amer. Chem. Soc.*, 87 (1965) 1241.
4 K. Schlögl and M. Walser, *Monatsh. Chem.*, 100 (1969) 1515.
5 S. I. Goldberg and J. S. Crowell, *J. Org. Chem.*, 29 (1964) 996; M. D. Rausch, *J. Org. Chem.*, 29 (1964) 1257; K. Yamakawa, N. Ishibashi and K. Arakawa, *Chem. Pharm. Bull. Jap.*, 12 (1964) 119.
6 K. Hata, I. Motoyama and H. Watanabe, *Bull. Chem. Soc. Jap.*, 37 (1964) 1719.
7 (a) M. Hadlington, B. W. Rockett and A. G. Nelhans, *J. Chem. Soc. C*, (1967) 1436;
(b) D. J. Booth and B. W. Rockett, *J. Chem. Soc. C*, (1968) 656.
8 L. Skattebøl and B. Boulette, *J. Organometal. Chem.*, 24 (1970) 547.
9 D. B. Denney and W. R. Davis, *J. Organometal. Chem.*, 24 (1970) 537.
10 D. J. Booth and B. W. Rockett, unpublished results.
11 D. J. Booth, G. Marr, B. W. Rockett and A. Rushworth, *J. Chem. Soc. C*, (1969) 2701.