Journal of Organometallic Chemistry, 396 (1990) 355–361
Elsevier Sequoia S.A., Lausanne
JOM 21150

Ethynylcobaltocenium compounds as precursors for bridged, heteronuclear oligometallocenes.

Preparation and reactions of ethynyl-, trimethylsilylethynyl- and ferrocenylethynylcobaltocenium salts

Michael Wildschek, Christopher Rieker, Peter Jaitner, Herwig Schottenberger and Karl Eberhard Schwarzhans *

Leopold Franzens Universität Innsbruck, Institut für Anorganische und Analytische Chemie, Innrain 52a, A-6020 Innsbruck (Österreich)

(Received April 4th, 1990)

Abstract

A general procedure for introducing substituents into cationic sandwich complexes by nucleophilic attack of suitable carbanions and subsequent hydride abstraction has been applied to the preparation of ethynyl-substituted cobaltocene species. Ethynylcobaltocenium hexafluorophosphate, trimethylsilylethynylcobaltocenium hexafluorophosphate, and salts of ferrocenylethynylcobaltocenium, a rigidly-bridged, conjugated heteronuclear bimetallocene, have been prepared. These compounds and isolated exo-diene intermediates have been characterized by NMR and IR spectroscopy, mass spectrometry and cyclic voltammetry. The new two-centered sandwich cation ferrocenylethynylcobaltocenium exhibits diamagnetism, indicating a situation not involving asymmetric averaging of the formal oxidation states on the NMR time scale. The electrochemical potentials and halfwave separations fall within the expected ranges.

Introduction

Compounds containing adjacent sandwich and half-sandwich metal centers, linked by conjugated or non-conjugated spacers continue to attract practical and theoretical interest [1–4]. In view of the remarkable valence averaging behaviour of some ethynebridged biferrocenes [5–7], there is an obvious interest in investigating related systems. Studies of the family of compounds containing alternating or mixed metals may improve understanding of charge and spin transfer phenomena, especially in relation to the predesigned lattice-independent inequivalence of their communicating redox sites.

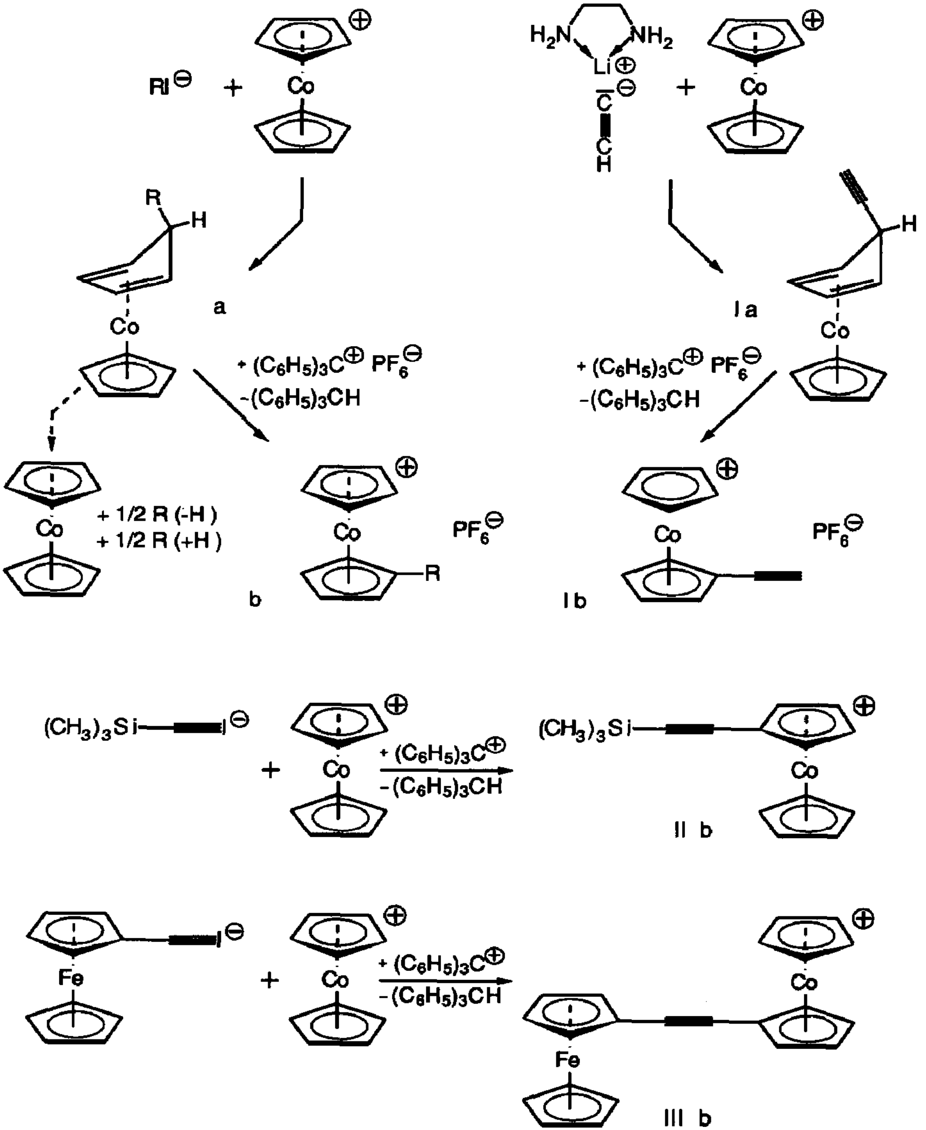
0022-328X/90/$03.50

Results and discussion

Chemical aspects

A convenient route to ethyne-bridged metallocenes via the corresponding biscyclopentadienylides has recently been reported [8]. However, such a statistical approach is inherently limited, particularly in the field of mixed metal compounds, since work-up presents difficulties and the yields are necessarily limited. Thus site-specific conversions of transition metal templates represent a valuable synthetic procedure (see Scheme 1).

Despite the occurrence of a predominant side reaction [9], the addition–elimination sequences allow widely variable combinations [9–11] because the nonpolar by-products are easy to separate from the desired salts. No systematic deprotona-



Scheme 1

tion studies, which could provide evidence of a non radical deprotonation–comproportionation pathway for the general side reaction have yet been carried out, but the remarkable stability of cobaltocene anion in various solvents when oxygen is excluded [12,13] seems to argue strongly in favour of such a pathway.

A second specific side reaction [14] between ferrocenylacetylenes and triphenylmethylium, which gives substituted indenes via stabilized vinyl cations, is also likely to influence yields, but mainly in systems involving less steric hindrance.

Theoretical aspects

Previous work has shown [15], that even a formal 18 + 18 electron system may exhibit intervalence transfer phenomena attributable to multiple interaction mechanisms. In particular the thermal onset of charge averaging is not solely affected by molecular features, but also by the solid state environment. Lattic dynamics has been shown to be altered by change in the external pressure [16] or by variation in the counter ion [17]. Crystallographic inequivalencies can also be responsible for a valence-trapped situation which cannot be attritubed to poor ligand-mediated interactions.

Intervalence behaviour can also be tuned to a certain extent by variation of the solvent [18]. Spectroscopic studies have been made of the properties of either isolated metal couples or of intermolecular interactions [19,20].

Results

As expected, cyclovoltammetric runs show quite similar potentials and halfwave separations for ferrocenylcobaltocenium hexafluorophosphate ($\Delta E_{1/2} = 1581$ mV) [21] and ferrocenylethynylcobaltocenium hexafluorophosphate. Within the conventional measuring ranges and at standard recording conditions the new analogous dimetallocenylethyne system also exhibits two reversible one electron waves with wide separation due to the actual potentials of the separate redox participants, but with slightly weaker infraction between them: $E_{\mathrm{fec}} = +637$ mV, $E_{\mathrm{coc}} = -776$ mV, $\Delta E_{1/2} = 1413$ mV (Ag/AgCl/Pt-ring/0.1 *M* $\mathrm{Bu_4N^+PF_6^-/CH_3CN}$).

The half wave potentials are shifted for the tetraphenylborate by 70 mV and 85 mV respectively; $E_{\mathrm{fec}} = +550$ mV, $E_{\mathrm{coc}} = -845$ mV, ($E_{\mathrm{BPh_4}} = +900$ mV). These electrochemical characteristics indicate the formation of electron donor- acceptor complexes with tetraphenylborate, which has been investigated in detail by spectroscopic methods [18–20]. In the case of fulvalene-bridged Fe–Co heterometallocene couples the recordability of standard ^{1}H NMR spectra is the first indication for diamagnetism [22]. The diamagnetism found for ferrocenylethynylcobaltocenium indicates that the charge of the monocation is located at the cobaltocene part.

Moessbauer data for differrocenylacetylene and [2.2] ferrocenophane 1,13-diyne [23] showed that the former monocation is of the mixed valence type and the latter is of the average valence type under normal measurements conditions. Thus one of the primary future goals should be the development of an efficient synthesis of the mixed Fe–Co–[2.2] metallocenophane 1,13-diyne for direct comparison.

Experimental

Physical measurements

Infrared spectra were recorded on Biorad Model FTS-40 or a Pye-Unicam model SP3-300 spectrometer of KBr moldings. ^{1}H NMR spectra were recorded on either a

Varian EM 360L (60 MHz) or like the ^{13}C spectra, on a Bruker AM-300 with tetramethylsilane as internal standard. Mass spectra were obtained with a MAT CH-7 mass spectrometer. CV-measurements were performed with a Wenking LT-78 potentiostate and a VSG 72 function generator. Ultrasonication involved use of a Bandelin Sonorex RK 255 S cleaning bath.

Compound preparation

Ethynylferrocene was prepared by a published procedure [24]. Ethynyltrimethylsilane, methyllithium (1.6 *M* solution in diethyl ether), n-butyllithium (2.0 *M* solution in hexane), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), lithium ethynylide ethylenediamine complex, and tritylium hexafluorophosphate were obtained commercially, and were used as purchased, except for TMEDA, which was distilled from sodium wire under nitrogen. All reactions were carried out under argon by standard Schlenk-tube techniques. Solvents were distilled from suitable drying agents prior to use. Most isolated compounds are moderately stable in air and, unless otherwise stated, may be purified with exposure to the air.

*(η^5-Cyclopentadienyl)[η^4-(*exo*-5-ethynyl)-1,3-cyclopentadiene] cobalt (Ia)*

To a suspension of 0.668 g (2.0 mmol) of cobaltocenium hexafluorophosphate in THF at 0 °C was added 0.184 g (2.0 mmol) of the lithium ethynylide TMEDA complex. The reaction mixture was sonicated for 15 min at 0 °C then the solvent was removed and the residue was taken up in hexane. The solution was filtered through Celite, and evaporated, and the residue was chromatographed on basic alumina (activity III) with hexane/diethyl ether 4/1 as eluent. Some 0.292 g (68%) of orange, spectroscopically pure, material was obtained.

^{1}H NMR ($CDCl_3$): δ 1.75 (d, 1H, $J = 1.7$ Hz), 2.67 (pseudo-q, 2H, $J = 1.9$ Hz), 3.33 (pseudo-q, 1H, $J = 1.9$ Hz), 4.68 (s, 5H), 5.23 (pseudo-t, 2H, $J = 1.9$ Hz). ^{13}C NMR ($CDCl_3$): δ 39.80 (d), 41.34 (d), 63.26 (d), 74.77 (d), 79.28 (d), 85.85 (s). IR (KBr): 3275, 3110, 3090, 3060, 2960, 2920, 1282, 1261, 1181, 1108, 1069, 1040, 1005, 810, 785, 650, 565, 500, 425 cm^{-1}. Mass spectrum: *m/z* 214 (100%)

Ethynylcobaltocenium hexafluorophosphate (Ib)

To a solution of 0.214 g (1 mmol) of Ia in 15 ml of methylene chloride was added a solution of 0.388 g (1 mmol) of trityliumhexafluorophosphate in 15 ml of methylene chloride. The mixture turned dark immediately. It was stirred for an additional 10 minutes. The solvent was removed in vacuo and the residue chromatographed on basic alumina (activity III) with a 3/1 mixture of diethyl ether/acetonitrile as eluent. After a yellow and a red band, Ib was eluted as broad yellow band, which after removal of the solvent in vacuo and drying gave 0.16 g (45%) of spectroscopically pure (Ib)

^{1}H NMR (CD_3CN): δ3.69 (s, 1H), 5.86 (pseudo-t, 2H, $J = 2.1$ Hz), 5.69(s, 5H), 5.90 (pseudo-t, 2H, $J = 2.1$ Hz). ^{13}C NMR (CD_3CN): δ74.88 (s), 84.97 (d), 85.89 (d), 86.00 (s), 87.43 (d), 87.57 (d) IR (KBr): 3275, 3125, 2128, 1455, 1420, 1397, 1075, 1048, 1040, 1015, 928, 835, 701, 678, 564, 520, 470, 445 cm^{-1}. Mass spectrum: *m/z* 213

*(η^5-Cyclopentadienyl)[η^4-(*exo*-5-trimethylsilylethynyl)-1,3-cyclopentadiene] cobalt (IIa)*

A solution of 0.108 g (0.155 ml, 1.1 mmol) of ethynyltrimethylsilane in 15 ml of dry dimethoxyethane (DME) was cooled to −15 °C and 0.50 ml of 2.0 *M* n-butyllithium solution (1 mmol) was added. The mixture was stirred at that temperature for 45 minutes then 0.334 g of cobaltocenium hexafluorophosphate (1 mmol) was added, and the resulting suspension was allowed to warm to room temperature and stirred for a further 2 hours, after which almost all the cobaltocenium had dissolved to give a clear red-orange solution. The solvent was removed in vacuo, and the residue taken up in n-pentane and chromatagraphed on basic alumina (activity III) with n-pentane as the eluent to give 0.186 g (65%) of orange IIa.

^{1}H NMR ($CDCl_3$): δ0.02 (s, 9H), 2.71 (pseudo-q, 2H, J ~ 1.9 Hz), 3.42 (pseudo-t, 1H, $J = 2.4$ Hz), 4.72 (s, 5H) 5.26 (pseudo-t, 2H, $J = 2$ Hz). ^{13}C NMR ($CDCl_3$): δ0.12 (q), 41.19 (d), 41.76 (d), 74.91 (d), 78.30 (s), 79.23 (d), 108.01 (s). IR (KBr): 3095, 3070, 2962, 2913, 2156, 1415, 1290, 1253, 1110, 1076, 1053, 1015, 903, 852, 844, 812, 660, 500 cm^{-1}. Mass spectrum: m/z 286 (100%).

Trimethylsilylethynyl-cobaltocenium hexafluorophosphate (IIb)

To a solution of 0.286 g (1 mmol) of IIa in 20 ml of methylene chloride 0.388 g (1 mmol) of tritylium hexafluorophosphate was added at room temperature and the mixture stirred for 15 minutes. The solvent was removed in vacuo and the residue was thoroughly washed first with diethyl ether, then with water, and finally again with diethyl ether, so that all non-polar reaction products and unreacted tritylium salt were removed. The product was dired in vacuo to yield 0.379 g (88%) of spectroscopically pure amber material.

^{1}H NMR (CD_3CN): δ0.25 (s, 9H), 5.65 (s, 5H), 5.67 (pseudo-t, 2H, $J = 2.1$ Hz), 5.83 (pseudo-t, 2H, J = 2.1 Hz). ^{13}C NMR (CD_3CN): $\delta - 0.59$ (q), 85.88 (d), 87.15 (d) 87.44 (d), 95.50 (s), 103.22 (s). IR (KBr): 3132, 2960, 2158, 1455, 1418, 1245, 830, 560 cm^{-1}. Mass spectrum: m/z 285 (40%).

η^5-Cyclopentadienyl) [η^4-(exo-5-ferrocenylethynyl-) 1,3-cylopentadiene] cobalt (IIIa)

A solution of 0.210 g (1 mmol) ethynylferrocene in 10 ml of dry DME was cooled in an ice bath to 0 ° C and 0.66 ml of a 1.6 M solution of methyllithium in diethyl ether (1 mmol) containing 0.23 ml (0.17 g, 1.5 mmol) of TMEDA were added. After 10 min stirring 0.334 g (1 mmol) of cobaltocenium hexafluorophosphate was added, and the mixture was allowed to warm to ambient temperature and stirred overnight. The solvent was removed in vacuo and the residue was chromatographed under an inert atmosphere on basic alumina with diethyl ether as eluent. A bright orange band was collected and yielded, after drying in vacuo, 0.319 g (80%) of pure IIIa.

^{1}H NMR ($CDCl_3$): δ2.79 (pseudo-q, 2H, J ~ 2.4 Hz), 3.50 (pseudo-t, 1H, J = 2.4 Hz), 4.04 (pseudo-t, 2H, $J = 1.9$ Hz), 4.09 (s, 5H), 4.21 (pseudo-t, 2H, $J = 1.9$ Hz), 4.75 (s, 5H), 5.29 (pseudo-t, 2H, $J = 2.0$ Hz). ^{13}C NMR ($CDCl_3$): δ40.91 (d), 42.36 (d), 66.15 (s), 68.04 (d), 69.75 (d), 71.11 (d), 73.61 (s), 74.83 (d), 79.20 (d), 88.10 (s). IR (KBr): 3090, 3057, 2963, 2924, 2210, 1260, 1104, 1069, 1039, 1022, 1000, 824, 807, 535, 512, 485, 459, 437 cm^{-1}. Mass spectrum: m/z 398 (100%)

Ferrocenylethynyl-cobaltocenium hexafluorophosphate (IIIb)

To a solution of 0.398 g (1 mmol) of IIIa 10 ml of dry methylene chloride at room temperature was added 0.388 g (1 mmol) tritylium hexafluorophosphate. The mixture was stirred for 15 min, the solvent was than removed in vacuo and the residue washed with diethyl ether, once with water, and again with diethyl ether until the washings were colourless. The dark purple material obtained was chromatographed on basic alumina (activity III) with a mixture of diethyl ether/acetonitrile 3/1 an eluent. Recrystallization from acetonitrile/diethyl ether gave 0.395 g (73%) of pure purple needles of IIIb.

^{1}H NMR (CD$_3$CN): δ4.29 (s, 5H), 4.41 (pseudo-t, 2H, $J = 1.9$ Hz) 4.58 (pseudo-t, 2H, $J = 1.9$ Hz), 5.67 (s, 5H), 5.69 (pseudo-t, 2H, $J = 2.1$ Hz), 5.85 (pseudo-t, 2H, $J = 2.1$ Hz). ^{13}C NMR (CD$_3$CN): δ71.23 (d), 71.34 (d), 73.02(d), 77.20 (s), 85.56 (d), 86.15 (d), 87.28 (d), 88.85 (s), 97.29 (s). IR (KBr): 3120, 2217, 2183, 1505, 1419, 1261, 1191, 1105, 1055, 1029, 1005, 983, 832, 701, 560, 505, 495, 462, 448 cm^{-1}. Mass spectrum; m/z 397 (45%). Melting point: 136 ° C.

Ferrocenylethynyl-cobaltocenium tetraphenylborate (IIIc)

The tetraphenylborate salt is most conveniently prepared by addition of a solution of IIIb in warm ethanol to a 5% ethanolic solution of sodium tetraphenylborate (10% molar excess). The mixture was cooled slowly to 0 ° C and the precipitate filtered off, washed twice with ethanol, and dried in vacuo. The product can be purified by column chromatography under the same conditions used for IIIb.

^{1}H NMR (CD$_3$CN): δ4.29 (s, 5H), 4.41 (pseudo-t, 2H, $J = 1.9$ Hz), 4.57 (pseudo-t, 2H, $J = 1.9$ Hz), 5.61 (s, 5H), 5.62 (pseudo-t, 2H, $J = 2.0$ Hz), 5.79 (pseudo-t, 2H, $J = 2.0$ Hz), 7.1 (mc, 20H). ^{13}C NMR (CD$_3$CN): δ71.25 (d) 71.33 (d), 73.03 (d), 77.21 (s), 85.50 (d), 85.87 (s), 86.11 (d), 87.23 (d), 122.8 (d), 126.6 (dxq), 131.1 (s), 136.8 (d). IR (KBr): 3100, 3058, 3000, 2218, 2183, 1580, 1500, 1480, 1430, 1415, 1109, 1070, 1053, 1032, 1005, 940, 859, 842, 820, 748, 735, 709, 565, 505, 470, 436 cm^{-1}.

Acknowledgements

We are grateful to colleagues of affiliated departments, Hubert Gstach and Hans Peter Kählig, Walter Mühlegger, and Ernst Müller, for recording the NMR spectra. We thank Karl Jäger for the mass spectral data and Dagmar Obendorf for performing the CV studies. We gratefully acknowledge financial support by the Austrian National Science Foundation, Fonds zur Fönderung der Wissenschaftlichen Forschung, under project number P 7592-CHE

References

1 U.T. Mueller-Westerhoff, Angew. Chem., 98 (1986) 700; Angew. Chem., Int. Ed. Eng., 25 (1986) 702, and references cited therein.
2 P. Härter, G. Boguth, E. Herdtwick, J. Riede, Angew. Chem. 98 (1989) 700; Int. Edition Engl., 28 (1989) 1008, and references cited therein
3 M.D. Rausch, W. Spink, B.G. Conway, R.D. Rogers, J.L. Atwood, J. Organomet. Chem., 383 (1990) 227, and references cited therein.
4 A.P. Kahn, D.A. Newman, K.P.C. Vollhardt, Synles 3 (1990) 141, and references cited therein.
5 K. le Vanda, D.O. Cowan, C. Leitch, K. Bechgaard, J. Am. Chem. Soc., 96 (1974) 6788.
6 C. le Vanda, K. Bechgaard, D.O. Cowan, J. Org. Chem., 41 (1976) 2700.
7 J.A. Kramer, D.N. Hendrickson, Inorg. Chem., 19 (1980) 3330.
8 E.E. Bunel, L. Valle, N.L. Jones, P.J. Carroll, M. Gonzalez, N. Munoz, J.M. Manriquez, Organometallics 7 (1988) 789.
9 H. Lehmkuhl, H.F. Nehl, Chem. Ber., 117 (1984) 3343.
10 C. Rieker, G. Ingram, P. Jaitner, H. Schottenberger, K.E. Schwarzhans, J. Organomet. Chem., 381 (1990) 127, and references cited therein.

11 G. Ingram, P.H. Jaitner, K.E. Schwarzhans, Z. Naturforsch., 45 b (1990) 781

12 N.M. Alpatova, L.L. Krishtalik, E.V. Ovsyannikova, E.V. Leonova, V.L. Shirokii, Elektrokhimiya, 25 (1989) 1341; CA: 111 (1989) 242435y, 242436z.

13 S.V. Kukharenko, E.M. Koldasheva, V.V. Strelets, Dokl. Akad. Nauk. SSSR, 303 (1988) 112, Chem. Abs. 110 (1989) 103776b.

14 T.S. Abram, W.E. Watts, J. Chem. Soc., Perkin Trans. I, (1977) 1527.

15 A. Gieren, K.E. Scharzhans, H. Schottenberger, C. Ruiz Perez, T. Hübner, X-Ray Diffractional Structure Determination of the "Mixed Valence"-Bimetallocenylene Ferrocenylene-Cobaltocenylenium Hexafluorophosphate and its Charge Distribution. Conference Meeting of German–Austrian Chemists; Innbruck, Austria (May 12–14, 1986) Abstract Bulletin, (1986) 78.

16 U. Sinha, M.D. Lowery, W.W. Ley, H.G. Drickamer, D.N. Hendrickson, J. Am. Chem. Soc. 110 (1988) 2471.

17 R.J. Webb, A.L. Rheingold, S.J. Geib, D.L. Staley, D.N. Hendrickson, Angew. Chem. 101 (1989) 1422; Angew. Chem., Int. Edition Eng., 28 (1989) 1388, and references cited therein.

18 R.L. Blackbourn, J.T. Hupp, J. Phys. Chem., 94 (1990) 1788.

19 S.F. Clark, R.J. Watts, D.L. Dubois, J.S. Conolly, J.C. Smart, Coord. Chem. Rev., 64 (1985) 273.

20 G.E. McMains, R.M. Nielson, M.J. Weaver, Inorg. Chem., 27 (1988) 1827.

21 K.E. Schwarzhans, W. Stolz, Monatsh. Chem., 118 (1987) 875.

22 K.E. Schwarzhans, H. Schottenberger, Z. Naturforsch., 3B (1983) 1496.

23 M. Watanabe, S. Iijima, I. Motoyama, H. Sanno, J. Phys., Colloq. (Orsa, Fr.) 2 (1979) 392.

24 T.S. Abram, W.E. Watts, Syn. React. Inorg. Metallorg. Chem., 6 (1976) 31, and references cited therein.