CHEMISTRY A European Journal



Accepted Article

Title: Mono- and Bimetallic Alkynyl Metallocenes and Half-Sandwich Complexes: A Simple and Versatile Synthetic Approach

Authors: Miguel A. Sierra; Luis Casarrubios; María C. De La Torre; Jose Luis García-Ruano; José Alemán; Carolina Valderas; Leyre Marzo

This manuscript has been accepted after peer review and the authors have elected to post their Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.201603462

Link to VoR: http://dx.doi.org/10.1002/chem.201603462

Supported by ACES



WILEY-VCH

Mono- and Bimetallic Alkynyl Metallocenes and Half-Sandwich Complexes: A Simple and Versatile Synthetic Approach

Carolina Valderas,^[a,b,c,†] Leyre Marzo,^[d,†] María C. de la Torre,^[b,c] José Luis García Ruano,^[d] José Alemán,^{*[d]} Luis Casarrubios,^[a,b] Miguel A. Sierra^{*[a,b]}

Dedicated to Prof. José María Marinas Rubio with the occasion of his retirement

Abstract: A general process for the synthesis of alkynyl mono and dimetallic metallocenes and half-sandwich complexes has been developed. This approach uses the addition of lithium derivatives of sandwich or half-sandwich complexes to arylsulfonylacetylenes. The reaction occurs in two steps (lithiation and anti-Michael addition to alkynylsulfone followed by elimination of the ArSO₂ moiety) to form the corresponding mono- or bimetallic alkynes in clearly higher yields, simpler experimental procedures, and more environmentally benign conditions than those of the so far reported for the synthesis of these type of products. The electrochemical properties of the newly obtained complexes have also been studied.

1-Metallocenyl- and half-sandwich substituted alkynes have profited as essential features or precursors of molecular wires,^[1] linked donor-acceptor arrangements,^[2] mixed valence compounds^[3] and related fields.^[4] For example, the fullerene derivative $\mathbf{A}^{^{[5]}}$ forms Fc-C60/Pd and bis-Fc-C60/Pd electroactive polymers, while $\boldsymbol{B}^{[6]}$ is a molecular switch controlled by light sources (top, Figure 1). It is also possible to find interesting metallocene compounds in biomedicine and analytical areas, as the derivative of BAPTA C,^[7] which selectively chelates Ca²⁺ ions that allows monitoring within cells, and compounds such as D,^{[8]e} which have been used to determine the concentration of bioactive compounds (such as L-ascorbic acid, tryptophan, Dpenicillamine, or dopamine) in pharmacological or biological samples (bottom-left, Figure 1). Additionally, structures having two metal centers, as E and F, are of great interest for obtaining "push-pull" systems (bottom-right).[9]

Despite the fact that these classes of organometallic derivatives are quite important, there are not efficient general

- [a] Dr. M. A. Sierra, Dr. C. Valderas, Dr. L. Casarrubios Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain. E-mail: (MAS) <u>sierraor@ucm.es</u>, www.biorganomet.es
- [b] Dr. M. A. Sierra, Dr. M. C. de la Torre, Dr. C. Valderas, Dr. L. Casarrubios. Centro de Innovación en Química Avanzada (ORFEO-CINQA)
- [c] Dr. M. C. de la Torre, Dr. C. Valderas Instituto de Química Orgánica General, Consejo Superior de Investigaciones Científicas (CSIC), Juan de la Cierva 3, 28006-Madrid, Spain
- [d] Dr. J. Alemán, Prof. Dr. J. L. García Ruano, Dr. L. Marzo Organic Chemistry Department, Universidad Autónoma de Madrid 28049-Madrid
- E-mail: jose.aleman@uam.es, www.uam.es/jose.aleman
 These authors contributed equally to the work reported in this paper.

Supporting information for this article is given via a link at the end of the document.



Figure 1. Relevant structure containing metallocene and half-sandwich substituted alkyne derivatives (Fc= ferrocenyl).

approaches for the synthesis of such as interesting compounds. Instead of them, their preparation requires, in general, multi-step synthesis mainly based in two different strategies, the cross-coupling of bromo- and iodo derivatives of the organometallic moiety with alkynyl stannanes,^[10] or alkynes,^[11] and the functionalization of the unsubstituted ethynyl organometallic derivatives^[12] (equations a and b, Scheme 1). Moreover, these approaches are not general (only valid when M= Fe, Ru), usually provide poor overall yields,^[13,14] and require the use of the scarcely ecofriendly transition metals as catalysts of the key steps. Thus, it is clear that a general method involving a shorter route (ideally one step) to access to ethynyl organometallic derivatives, flexible enough to allow the synthesis of different metallocene- and half-sandwich monometallic and bimetallic derivatives, is desirable

Recently, we have reported the electrophilic behavior of arylsulfonylacetylenes with organolithiums through an unusual aattack (anti-Michael addition) followed by elimination of the ArSO₂ moiety to allow the alkynylation of lithiated sp² and sp³ carbon atoms, yielding the corresponding alkynes.^[15] Based on these results, we envisioned the possibility of using lithium in reactions with arylsulfonylacetylenes metallocenes (commercially available or easily prepared in one step from alkynes^[16]) as a general method for obtaining the coupling of alkynyl and metallocenyl moieties (equation c, Scheme 1). In this work, we present the results obtained in this research which has provided different alkynyl metallocenes, half-sandwich derivatives, and bis-metallocenyl alkynes. The clear advantages of our procedure with respect to those so far reported, concerning experimental simplicity, conditions and yields determine our reaction must be considered as the method of choice for preparing these important class of compounds. Finally, some interesting electrochemical properties of these compounds will be presented.

WILEY-VCH

10.1002/chem.201603462



Scheme 1. Different general approaches for the synthesis of alkynyl halfsandwich and metallocenes.

We initiate the study with the preparation of different ferrocenyl alkynes. Ferrocenyl lithium is easily available by treatment of ferrocene with ^tBuLi at 0 °C in a 1:1 THF/pentane mixture. Lithium derivative of ferrocene was reacted with a twofold excess of phenylethynyl sulfone 2a, cleanly affording the corresponding phenylethynyl ferrocene 3Aa in a 69% isolated yield in few minutes. In comparison to the previous work, the reaction of 2a with phenyl-lithium was instantaneous at -78 °C, which indicates a lower reactivity of the ferrocenyl lithium derivative.^[15] This reaction was general for aryl-substituted sulfones (Table 1) having both electron donor (2Ab-Ad) or electron withdrawing substituents (2Ae and 2Af). From moderate to good yields in the corresponding arylalkynyl ferrocenes were obtained in all cases. On the contrary, tBu and Cy acetylene derivatives 1g and 1h led complicated crude mixtures in which Michael type products could be identified. Finally, ethynyl ferrocene 3Ai was obtained in a two-step sequence (69% overall yield) starting from the TIPS-alkynyl sulphone 2i followed by direct desilylation of TIPSethynylferrocene (TBAF/THF). Table 1. Reaction of ferrocenyl lithium with different arylethynyl-suflones $2^{[a]}$



[a] Reactions were carried out at -78 ^{o}C with 0.2 mmol of sulfone 1 and 0.4 mmol of the lithium ferrocene derivative.[b] Direct desilylation by TBAF was

employed before isolation (see supporting information). (n.r.= no reaction, see text).

Analogous Li-ruthenocene and Li-osmacene were obtained from the corresponding metallocenes **2B** and **2C**, following the procedure optimized for ferrocene (*t*BuLi at 0°C in a 1:1 THF/pentane mixture). They were subsequently reacted with phenylethynyl sulfone **2a** at 0 °C. Although the conversion to both phenylethynyl metallocenes was quantitative by ¹H NMR, ruthenocene derivative **3Ba** was isolated in 71% yield, and the osmacene derivative **3Ca** in 30% yield, due to extensive decomposition during the chromatography purification (Table 2). The lithiation of manganocene **2D** was not possible in our hands, and only decomposition products were detected by reaction with the acetylene **1a**.^[17]





[a] Reactions were carried out at -78 or 0 °C with 0.2 mmol of sulfone **1a** and 0.4 mmol of the lithium derivative [b] Lithiation process was not possible, only decomposition products were found in the crude mixture.

The preparation of half-sandwich Re and Mn ethynyl derivatives was next attempted. Complexes **2E-F** were lithiated under the above mentioned conditions and the corresponding Liderivatives reacted with sulfone **2a**. In both cases ¹H NMR showed complete conversion into the desired phenylethynyl half-sandwich derivatives, but the isolated yields for compounds **3Ea** and **3Fa** were 62% and 57% (Table 3). Under similar conditions (addition of *n*-BuLi at -78 °C and treatment with **1a** at -78 °C), tricarbonyl (η^6 -phenyl)chromium (0) was transformed into the ethynyl complex **3Ga** with a 56% yield. Therefore, this approach is also suitable for the preparation of alkynyl derivatives of half-sandwich complexes.^[18]

Table	3.	Reaction	of	mono-sandwich	lithium	derivatives	with	the
phenyl	ethyr	nyl-sulfone	1a. ^[a]					

OC [·] M·CO 2E-F	1) <i>n</i> -BuLi, 0 °C, THF/pentane (1:1) 2) PhSO ₂ Tol 1a THF, 0 °C.	OC' ^M .CO 3Ea-Ga
Mn(CO) ₃ 3Ea 62%	Ph Re(CO) ₃ Ph 3Fa 57%	$ \begin{array}{c} \hline $

[a] Reactions were carried out at -78 or 0 °C with 0.2 mmol of sulfone **1a** and 0.4 mmol of the lithium derivative [b] Both steps were carried out at – 78 °C and THF as solvent.

WILEY-VCH

10.1002/chem.201603462

Hetero-bimetalocenyl alkynes, having the two metallocenes bridged through one ethynyl moiety were next studied. Thus, ferrocenylethynyl sulfone **1j** (prepared from **3Ai**) was reacted with ruthenocenyl lithium **2B**. The resulting Fe-Ru heterobimetallic compound **3Bj** was very unstable and it could be isolated only in a 20% yield. Analogously, the reaction of sulfone **1j** with the lithium reagent derived from Cp(CO)₃Re (**2F**-**Li**) yielded the heterobimetallic Fe-Re derivative **3Fj** in a respectable 50% isolated yield (Scheme 2). The applicability of this approach to prepare heterobimetallic complexes was thus demonstrated.



Scheme 2. Synthesis of heterobimetallic complexes **3Bj** and **3Fj** from alkynyl sulfone **1***j*.

Being aware of the wide use of ethynyl ferrocene as an electrochemical marker, ^[19] and the easiness of our methodology that allow the easy incorporation of a wide range of aromatic groups to the ethynyl sandwich derivatives (**3Aa-Af**) and flexible entry developed above to diverse types of half-sandwich derivatives (**3Ea-3Ga**) and heterobimetallic complexes (**3Bj-3Fj**), we decided to undertook a systematic study of their electrochemical properties.



Figure 2. The electrochemical behavior of arylethynylferrocenes 3Aa-Af.

The electrochemical behavior of arylethynylferrocenes **3Aa-Af** was first considered. In all cases room temperature (rt) 10⁻³ solutions in MeCN as solvent and 0.1M NBu₄ClO₄ as supporting electrolyte were used to register the cyclic voltammograms of complexes **3Aa-Af**. Figure 2 and Table 4 collect the results

obtained. Complexes **3Aa-Af** showed a single reversible oxidation event assigned to the Fe(II) – Fe(III) process. As expected, due to the low conjugation of the phenyl ring with the ferrocene moiety, the substitution in the aromatic ring resulted in a low influence in the oxidation potential of the complex (0.61-0.68 V, compared to 0.66 V for ethynyl ferrocene). Nevertheless, complexes **3Aa-3Ad** having donor substituents in the *p*-position of the aromatic ring showed lower oxidation values than complexes **3Ae** and **Ae** having electron withdrawing substituents. Albeit small, this effect should probably be due to the stabilization of the ferrocenium radical-cation formed during the oxidation event.

Table 4.	The	electrochemical	data of a	rvlethvn	vlferrocenes	3Aa-Af. ^[a]
4010 41		0100011001110001	uulu ol u		,	0/10//11

Entry	Compound (R)	<i>E</i> _{pa} (V)	E _{pc} (V)	<i>E</i> _{p1/2} (V)
1	3Aa (H)	0.66	0.56	0.10
2	3Ab (4-Me)	0.65	0.57	0.08
3	3Ac (4-OMe)	0.61	0.53	0.08
4	3Ad (2,4,5-triMe)	0.68	0.56	0.12
5	3Ae (4-CF ₃)	0.66	0.48	0.18
6	3Af (2-CI)	0.68	0.47	0.21

[a] Recorded at rt in MeCN using 0.1 M [NBu₄]ClO₄ as supporting electrolyte and Ag/AgCl 3M as reference and a Pt wire counter electrode (scan rate 0.1 V/s).

Electrochemical data for half-sandwich complexes **3Ea** and **3Fa** are presented in Figure 3. An irreversible oxidation wave at 1.30 V (Re complex **3Ea**) and 1.34 V (Mn complex **3Fa**), is in good agreement for the described oxidation values of not substituted complexes (1.16 V relative to Fc/Fc⁺ for CpRe(CO)₃^[20] and 0.92 V related to Fc/Fc⁺ for CpMn(CO)₃^[21,22]). In both cases, the oxidation wave is assigned to the formation of **3Ea** and **3Fa** respectively. It is known that these species have a strong tendency to dimerize, making this process irreversible.^[20-22]



Figure 3. The electrochemical behavior of arylethynylferrocenes 3Ea-3Fa.

WILEY-VCH

10.1002/chem.201603462

A comparative study of the redox behavior of alkynyl sandwich complexes was performed for complexes **3Aa**, **3Ba** and **3Ca**. The results are shown in Figure 4 and Table 5 (cyclic and square wave voltamperometry). Thus, while complexes ferrocene **3Aa** and ruthenoce **3Ba** showed a quasi-reversible behavior ($\Delta p = 0.10$ V and 0.15 V, respectively), the osmocene derivative **3Ca** was found with a clearly irreversible wave ($\Delta p = 0.41$ V). These results are congruent with those reported in the literature.^[22]



Figure 4. Comparison in the electrochemical behavior of 3Aa, 3Ba and 3Ca. Table 5. The electrochemical data of 3Aa, 3Ba and 3Ca.^[a]

Entry	Compounds	E _{pa} (V)	<i>E</i> _{pc} (V)	<i>E</i> _{p1/2} (V)
1	3Aa	0.66	0.56	0.61
2	3Ba	0.85	0.70	0.77
3	3Ca	0.79	0.38	0.85

[a] Recorded at rt in MeCN using 0.1 M [NBu₄]ClO₄ as supporting electrolyte and Ag/AgCl 3M as reference and a Pt wire counter electrode (scan rate 0.1 V/s).

Bimetallic Fe-Ru **3Bj** and Fe-Re **3Fj** complexes have an electrochemical imprint almost identical to the overlapping of the corresponding monometallic complexes (Figure 5), which clearly indicates a lack of communication between the two metals of the molecule. Both complexes showed a cathodic displacement of 0.11 V in the reversible Fe oxidation of the Fe-Ru complex **3n** and an analogous shift of 0.05 V in the irreversible wave of the Ru. These small variations may be explained by the stabilizing effect of the second metal over the cation (first oxidation wave) and the double cation (second oxidation wave) with respect to the monometallic complexes. In the Fe-Re complex these differences are even lower (0.03 and 0.02 V, respectively) than in its Fe-Ru congeners.

To conclude, a general protocol to access to sandwich and half-sandwich alkynyl derivatives, including heterobimetallic derivatives has been developed. This approach makes use of the addition of lithium derivatives of sandwich or half-sandwich complexes and arylsulfonylacetylenes. The process is general and tolerates different substituents at the alkyne moiety. When compared with the usual methods for the synthesis of these type of attractive products, our sequence produces better yields in easier experimental procedures without the use of expensive transition metals or toxic reagents. The electrochemical properties of the newly obtained complexes have been studied. For arylethynyl ferrocenes the influence of the substituents in the oxidation wave attributed to the Fc/Fc^+ one electron oxidation is negligible showing a lack of communication between the aryl group and the metal center. A similar behavior is encountered in bimetallic Fe-Ru **3Bj** and Fe-Re **3Fj** complexes, which have an electrochemical imprint almost identical to the overlapping of the corresponding monometallic complexes.

3Aa 3Ba 1.0x10⁻⁴ 3Bj solvent: MeCN 8.0x10 6.0x10 4,0x10 Ř 2.0x10 0,0 -2.0x10 -4,0x10⁻⁴ 0.0 0,5 1,0 1.5 2.0 E/V - 3Aa ____ 3Fa _ 3Fi 1.2x10 solvent: MeCN 1,0x10 8,0x10 6,0x10 NA. 4,0x10 2.0x10 0.0 -2,0x10 0.0 1,0 1.5 2.0 0.5 EΛ

Figure 5. The electrochemical behavior of heterobimetallic complex 3Bj and comparison with 3Aa and 3Ba (top) and 3Fj with 3Fa and 3Aa (bottom).

Acknowledgements

Support for this work under grants (CTQ2015-64561-R to JA CTQ2013-46459-C2-01-P to MAS; CTQ2013-46459-C2-02-P to MCT, CTQ2014-51912-REDC Programa Redes Consolider) from the MINECO (Spain) is gratefully acknowledged.

Keywords: acetylene sulfones • metallocenes • anti-Michael • Half-Sandwich Complexes

 [1] Examples a) Y. Li, M. Josowicz, L. M. Tolber, J. Am. Chem. Soc. 2010, 132, 10374; b) F. Chen, N. J. Tao, Acc. Chem. Res. 2009, 42, 429; b) C. Wang, L.-O. Plsson, A. S. Batsanov, M. R. Bryce, J. Am. Chem. Soc. 2006, 128, 3789.

- [2] a) G. Laus, C. E. Strasser, M. Holzer, K. Wurst, G. Pürstinger, K. H. Ongania, M. Rauch, G. Bonn, H. Schottenberger, *Organometallics* 2005, *24*, 6085; b) M. Pizzotti, R. Ugo, C. Dragonetti, E. Annoni, *Organometallics* 2003, *22*, 4001; c) S. Barlow, S. Marder, *Chem. Commun.* 2000, 1555, and the pertinent references therein.
- [3] a) Mixed Valence Compounds, ed. D. B. Brown, Reidel Publishing Company, Dordrecht, Holland, 1980; b) D. Astruc, *Electron Transfer* and Radical Processes in Transition-metal Chemistry, VCH, New York, 1995.
- [4] a) M. S. Inkpen, T. Albrecht, N. J. Long, *Organometallics* 2013, *32*, 6053; b) T. Kitagawa, H. Matsubara, K. Komatsu, K. Hirai, T. Okazaki, T. Hase, *Langmuir* 2013, *29*, 4275.
- [5] M. Wysocka-Zołopa, K Winkler, R. Caballero, F. Langa, *Electrochimica Acta*, 2011, 56, 5566.
- [6] S. Muratsugu, M. Kishida, R. Sakamoto, H. Nishihara, *Chem. Eur. J.* 2013, *19*, 17314.
- [7] K. X. Bhattacharyya, L. Boubekeur-Lecaque, I. Tapsoba, E. Maisonhaute, B. Schöllhorn, C. Amatore, *Chem. Commun.* 2011, 47, 5199.
- [8] a) J.-B. Raoof, R. Ojani, H. Karimi-Maleh Bull. Chem. Soc. Ethiop. 2008, 22, 173; b) J.-B. Raoof, R. Ojani, R. Hosseinzadeh, V. Ghasemi, Analytical Sciences, 2003, 19, 1251; c) J.-B. Raoof, R. Ojani, Hn Karimi-Maleh, Electroanalysis, 2008, 11, 1259; d) J.-B. Raoof, R. Ojani, F. Chekin, R. Hossienzadeh, Int. J. Electrochem. Sci., 2007, 2, 848; e) M. Liu, L. Wang, J. Deng, Q. Chen, Y. Li, Y. Zhang, H. Li, S. Yao, Analyst, 2012, 137, 4577; f) M. Liu, L. Wang, Y. Meng, Q. Chen, H. Li, Y. Zhang, S. Yao, Electrochimica Acta, 2014, 116, 504.
- [9] For Ru and Fe, see: a) S. Kato, M. Kivala, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht, F. Diederich, *Chem. Eur. J.* 2009, *15*, 8687; b) M. Sato, Y. Kubota, Y. Kawata, T. Fujihara, K. Unoura, A. Oyama, *Chem. Eur. J.* 2006, *12*, 2282; c) A. Korotvicka, I. Cisarova, J. Roithova, M. Kotora, *Chem. Eur. J.* 2012, *18*, 4200; d) Y. Masuda, C. Shimizu, *J. Phys. Chem.* 2006, *110*, 7019; e) K. Kaleta, F. Strehler, A. Hildebrandt, T. Beweries, P. Arndt, T. Rüffer, A. Spannenberg, H. Lang, U. Rosenthal, *Chem. Eur. J.* 2012, *18*, 12672; f) L. Becker, F. Strehler, M. Korb, P. Arndt, A. Spannenberg, W. Baumann, H. Lang, U. Rosenthal, *Chem. Eur. J.* 2014, *20*, 3061; Para compuestos de Re y Mn véase: g) A. S. Romanov, J. M. Mulroy, M. Y.Antipina, T. V. Timofeeva, *Acta Cryst.* 2009, *C65*, m431.
- [10] C. L. Sterzo, J. K. Stille, Organometallics 1990, 9, 687.
- See, among others: a) V. P. Dyadchenko, M. Dyadchenko, V. N. Okulov, D. A. Lemenovskii, *J. Organomet. Chem.* 2011, 696, 468; b) L. A. Hore, C. J. McAdam, J. L. Kerr, N. W. Duffy, B. H. Robinson, J. Simpson, *Organometallics* 2000, 19, 5039; c) J.K. Pudelski, M. R. Callstrom, *Organometallics* 1994, 13, 3095.
- [12] Representative examples: a) E. R. Young, J. Rosenthal, D. G. Nocera, *Chem. Sci.* 2012, *3*, 455; b) F. Lutz, T. Kawasaki, K. Soai, *Tetrahedron: Asymmetry* 2006, *17*, 486; b) P. Stepnicka, R. Gyepes, I. Cisarová, V. Varga, M. Polásek, M. Horácek, K. Mach, *Organometallics* 1999, *18*, 627.
- [13] For the synthesis via Corey-Fuchs/Ohira and Sonogashira reaction, see: a) M. Laskoski, W. Steffen, M. D. Smith, U. H. F. Bunz Chem. Commun., 2001, 691; b) J. C. Torres, R. A. Plli, M. D. Vargas, F. A. Violante, S. J. Garden, A. C. Pinto, Tetrahedron, 2002, 58, 4487; c) M. Laskoski, W. Steffen, J. G. M. Morton, M. D. Smith, U. H. F. Bunz, Angew. Chem. Int. Ed. 2002, 41, 2378; d) M. Laskoski, W. Steffen, J. G.

M. Morton, M. D. Smith, U. H. F. Bunz, *J. Organometallic Chem.* **2003**, 673, 25; e) U. Siemeling, J. V. der Brüggen, U. Vorfeld, B. Neumann, A. Stammler, H.-G. Stammler, A. Brockhinke, R. Plessow, P. Zanello, F. Laschi, F. Fabrizi de Biani, M. Fontani, S. Steenken, M. Stapper, G. Gurzadyan, *Chem. Eur. J.* **2003**, *9*, 2819.

- [14] a) R. Sun, H. Wang, J. Hu, J. Zhao, H. Zhang, Org. Biomol. Chem.
 2014, 12, 5954; Ethynylferrocene can be prepared following the Negishi's method for the conversion of a ketone into an acetylenic group in a one-pot synthesis. The reported yield for this approach is 80%. However, in our hands, consistently lower yields (around 50-60%) were obtained. See: b) G. Disneau, G. Balavoine, T. Fillebeen-Khan, J. Organomet. Chem. 1992, 425, 113; Another synthesis from formylferrocene has also been reported: c) J. G. Rodríguez, A. Oñate, R. M. Martín-Villamil, I. Fonseca, J. Organomet. Chem. 1996, 513, 71.
- [15] a) J. L. García Ruano, J. Alemán, L. Marzo, C. Alvarado, M. Tortosa, S. Díaz-Tendero, S. Fraile, *Angew. Chem. Int. Ed.* **2012**, *51*, 2712; b) J. L. García Ruano, J. Alemán, L. Marzo, C. Alvarado, M. Tortosa, S. Díaz-Tendero, S. Fraile, *Chem. Eur. J.* **2012**, *18*, 8414; c) L. Marzo, I. Pérez, F. Yuste, J. Alemán, J. L. García Ruano *Chem. Commun.* **2015**, *51*, 346.
- [16] J. Meesin, P. Katrun, C. Pareseecharoen, M. Pohmakotr, V. Reutrakul, D. Soorukram, C. Kuhakarn, J. Org. Chem. 2016, 81, 2744.
- [18] In comparison with other methods, e.g., the complex **3Ea** was obtained with a moderate yield (30%), using a copper acetylene derivative, and the previous synthesized iodo-manganacene derivative.(see: L. Asatiani, V. Rtskhyladze, *Seriya Khimicheskaya*, **1996**, *22*, 59:

- [19] Selected recent examples: a) Carbon nanotubes: M. Coates, S. Griveau, F. Bedioui, T. Nyokong, *Electroanalysis* 2012, 24, 1833; b) Carbon nanofibers: E. C. Landis, R. Hamers, J. Chem. Mater. 2009, 21, 724; d) "Glassy" carbon: M. V. Sheridan, K. Lam, W. E. Geiger, J. Am. Chem. Soc. 2013, 135, 2939; e) conductive diamond: R. E. Ruther, Q. Cui, R. J. Hamers, J. Am. Chem. Soc. 2013, 135, 5751; f) Metallic surfaces (Au, Pt): M. V. Sheridan, K. Lam, W. E. Geiger, Angew. Chem. Int. Ed. 2013, 52, 12897; g) Nucleosides: P. Brázdilová, M. Vrábel, R. Pohl, H. Pivonková, L. Havran, M. Hocek, M. Fojta, Chem. Eur. J. 2007, 13, 9527. h) M. Valencia, M. Martín-Ortiz, M. Gómez-Gallego, C. Ramírez de Arellano, M. A. Sierra, Chem. Eur. J. 2014, 20, 3831.
- [20] a) D. Chong, A. Nafady, P. J. Costa, M. J. Calhorda, W. E. Geiger, J. Am. Chem. Soc. 2005, 127, 15676; b) D. Chong, D. R. Laws, A. Nafady, P. J. Costa, A. L. Rheingold, M. J. Calhorda, W. E. Geiger, J. Am. Chem. Soc. 2008, 130, 2692.
- [21] D. R. Laws, D. Chong, K. Nash, A. L. Rheingold, W. E. Geiger, J. Am. Chem. Soc. 2008, 130, 9859.
- [22] For a revision of the electrochemistry of half sandwich complexes, see: W. E. Geiger, Coord. Chem. Rev. 2013, 257, 1459.

WILEY-VCH

Entry for the Table of Contents (Please choose one layout)

COMMUNICATION



A general process for the synthesis of alkynyl mono and dimetallic metallocenes and half-sandwich complexes has been developed. This approach uses the addition of lithium derivatives of sandwich or half-sandwich complexes and arylsulfonylacetylenes. Carolina Valderas, Leyre Marzo, María C. de la Torre, José Luis García Ruano, José Alemán*, L. Casarrubios, Miguel A. Sierra*

Page No. – Page No.

Mono- and Bimetallic Alkynyl Metallocenes and Half-Sandwich Complexes: A Simple and Versatile Synthetic Approach