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Novel Ruthenium- or Iron-Containing Tetraynes as Precursors of Mixed-Metal Oligomers

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Summary: The preparation of the novel carbon-rich iron- and ruthenium-containing tetraynes **3** *and* **5** *from* $HC{\equiv}CC_6H_4C{\equiv}CSi^iPr_3$ (**2**)*, via catalyzed C−C coupling and ruthenium−vinylidene activation, is described. Their desilylated products* **4** *and* **6***, which possess two π-conjugated "rod"-shaped arms and C≡CH hands, have been used as monomers for access to novel mixed* d^6/d^8 *metal containing rigid and flexible units (***7** *and* **8***) or unidimensional (***9***) oligomers.*

Carbon-rich organometallics containing rigid, π-conjugated chains are currently attracting interest for use in the synthesis of unsaturated organic molecules, oligomers,[1,2] or organometallic polymers[3] and for access to novel bimetallic systems with π-conjugated bridges suitable for electron transfer.[4,5] Homometallic oligomers or polymers have been made *via* C−H bond activation with rhodium[6] or from alkynyltin derivatives.[7] Those that contain rigid bridges have showed interesting nonlinear optical,[8] liquid crystal,[9,10] or magnetic[11] properties. In contrast, mixed-metal polymers containing organic linkages are rare and involve d^8/d^8 systems: Pt/Pd and Ni/Pt.[12] This is due to the difficult preparation of suitable monomers or the lack of efficient polymer synthesis, despite interest in their electron transfer properties and in their use as unidimensional materials or catalyst precursors.

We now report (i) an efficient access to two novel organometallic tetraynes which possess two carbon-rich rigid *arms* with terminal C≡CH *hands*, *via* two C−C and M−C couplings of the $^iPr_3SiC{\equiv}CC_6H_4C{\equiv}CH$ group followed by selective desilylation, and (ii) their use in selective access to the first d^6/d^8 Fe/Pd-, Fe/Ni-, and Ru/Pd-containing oligomers.

The red unsaturated ferrocene derivative **3** was made in 65% yield by catalytic coupling of 1,1′-diiodoferrocene[13] (**1**; 5.6 mmol) and 1-((triisopropylsilyl)ethynyl)-4-ethynylbenzene (**2**; 12.3 mmol) with $PdCl_2(PPh_3)_2$/$Cu(OAc)_2$ catalysts (0.45 mmol) in HN^iPr_2 at 90 °C for 16 h. Compound **3** (^{13}C NMR (δ, ppm) 106.84 (s, $C{\equiv}\mathit{C}{-}Si$), 92.49, 89.46, and 86.33 (s, $Ru{-}\mathit{C}{\equiv}\mathit{C}C_6H_4$-$\mathit{C}{\equiv}CSi$)] was desilylated by treatment with $(Bu^n{}_4N)F\cdot xH_2O$ in THF, leading a good yield (85%) of the red iron tetrayne derivative **4** with equivalent C≡CH ends (^{13}C NMR (δ, ppm) 89.37 and 86.36 (s, $Ru{-}\mathit{C}{\equiv}\mathit{C}C_6H_4$-$C{\equiv}CH$), 83.43 (d, $\mathit{C}{\equiv}CH$, $^2J_{CH}$ = 49.80 Hz), 78.65 (d, $C{\equiv}\mathit{C}H$, $^1J_{CH}$ = 249.00 Hz)) (Scheme 1).

As *cis*-$RuCl_2(dppe)_2$[14] was shown to lead to Ru−C≡C linkages via ruthenium vinylidene intermediates,[15] *cis*-$RuCl_2(dppe)_2$[14] (0.43 mmol) was reacted with the diyne **2** (1.28 mmol) in the presence of $NaPF_6$ (1.28 mmol) with an excess of NEt_3 (3.44 mmol), which led to the formation at room temperature (20 h) of the bis(alkynyl)ruthenium complex **5** (80%). Complex **5** ($^{31}P\{^1H\}$ NMR (δ, ppm) 54.14 (s, dppe); $^{13}C\{^1H\}$ NMR (δ, ppm) 136.80 (quint, Ru−C, $^2J_{PC}$ = 10.6 Hz), 130.66 (s, $Ru{-}C{\equiv}\mathit{C}$), 108.42 (s, $\mathit{C}{\equiv}CSi$), 89.78 (s, $C{\equiv}\mathit{C}Si$)) was desilylated with $(Bu^n{}_4N)F\cdot xH_2O$ in THF, leading to the yellow monomer **6** (95%) ($^{31}P\{^1H\}$ NMR (δ, ppm) 54.08 (s, dppe); ^1H NMR (δ, ppm) 3.10 (s, C≡CH); $^{13}C\{^1H\}$ NMR (δ, ppm) 136.75 (quint, Ru−C, $^2J_{PC}$ = 10 Hz), 131.09 (s, $Ru{-}C{\equiv}\mathit{C}$), 84.84 (s, $\mathit{C}{\equiv}CH$), 76.84 (s, $C{\equiv}\mathit{C}H$); ^{13}C NMR

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(1) Bunz, U. H. F. *Angew. Chem.* **1994**, *106*, 1127−1130; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1073−1076.

(2) Diederich, F.; Rubin, Y. *Angew. Chem.* **1992**, *104*, 1123−1145; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101−1123.

(3) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1981**, *41*, 149−179.

(4) (a) Le Narvor, N.; Lapinte, C. *Organometallics* **1995**, *14*, 634−639. (b) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129−7138. (c) Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411−4412.

(5) (a) Weng, W.; Bartik, T.; Gladysz, J. A. *Angew. Chem.* **1994**, *106*, 2272−2276; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2199−2202. (b) Brady, M.; Weng, W.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2655−2656.

(6) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188−190.

(7) (a) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187−188. (b) Ingham, S. L.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1994**, *470*, 153−159. (c) Faulkner, C. W.; Ingham, S. L.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1994**, *482*, 139−145.

(8) (a) Marder, S. R. In *Inorganic Materials*; Bruce, D. W., O'Hare, D., Eds.; Wiley: New York, 1992; pp 115−164. (b) Frazier, C. C.; Guha, S.; Chen, W. P.; Cockerham, M. P.; Porter, P. L.; Chauchard, E. A.; Lee, C. H. *Polymer* **1987**, *28*, 553−555. (c) Fyfe, H. B.; Mlekuz, M.; Stringer, G.; Taylor, N. J.; Marder, T. B. In *Inorganic and Organometallic Polymers With Special Properties*; NATO ASI Series E; Laine, R. M., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. 206, pp 331−344.

(9) (a) Altmann, M.; Bunz, U. H. F. *Angew. Chem.* **1995**, *107*, 603−605; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 569−571. (b) Altmann, M.; Bunz, U. H. F. *Macromol. Rapid Commun.* **1994**, *15*, 785. (c) Altmann, M.; Bunz, U. H. F. *Adv. Mater.* **1995**, *7*, 726−728.

(10) Dembek, A. A.; Burch, R. R.; Feiring, A. E. *J. Am. Chem. Soc.* **1993**, *115*, 2087−2089.

(11) Hmyene, M.; Yassar, A.; Escorne, M.; Percheron-Guegan, A.; Garnier, F. *Adv. Mater.* **1994**, *6*, 564−567.

(12) (a) Sonogashira, K.; Kataoka, S.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *160*, 319−327. (b) Sonogashira, K.; Ohga, K.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1980**, *188*, 237−243.

(13) Kovar, R. F.; Rausch, M. D.; Rosemberg, H. *Organomet. Chem. Synth.* **1970/71**, *1*, 173.

(14) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635−1639.

(15) Touchard, D.; Morice, C.; Cadierno, V.; Haquette, P.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1994**, 859−860.

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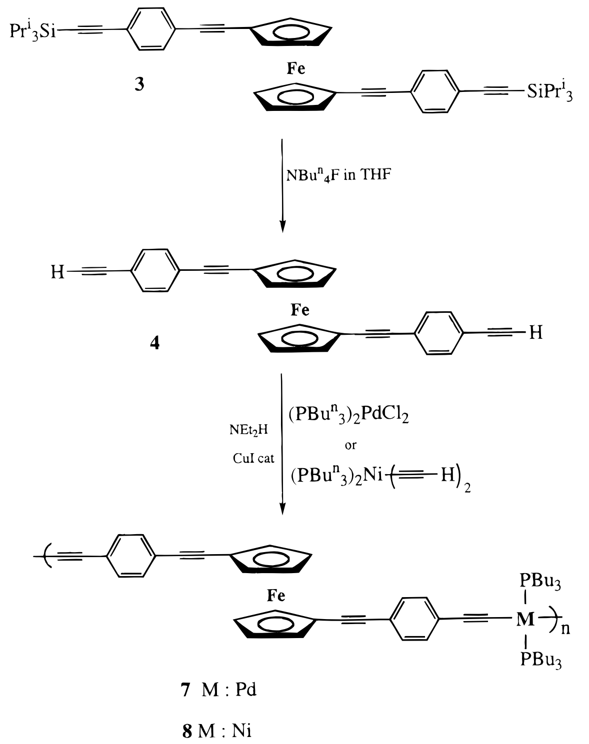
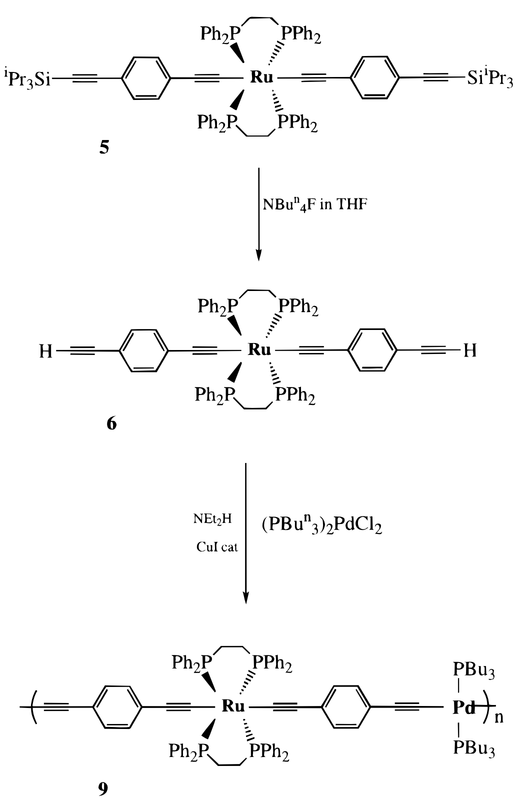
Scheme 1



Scheme 2



(δ, ppm) 84.84 (d, $C{\equiv}$CH, $^2J_{CH}$ = 42.73 Hz), 76.84 (d, C$\equiv C$H, $^1J_{CH}$ = 249.00 Hz) (Scheme 2).

It is noteworthy that the formation of monomers **4** and **6** could also be obtained directly by reaction of an excess of 1,4-diethynylbenzene and 1,1′-diiodoferrocene or *cis*-RuCl$_2$(dppe)$_2$ under conditions similar to those leading to **3** or **5**. However, the monomers **4** and **6** were always contaminated with oligomeric products which could not be separated, and this direct route to **4** and **6** has to be avoided.

The monomers **4** and **6** have been used to produce heterobimetallic oligomers **7**–**9** *via* the classical copper(I) catalytic reaction for the transformation RC$\equiv$CH + MX + NR$_3$ → RC$\equiv$CM + HNR$_3{}^+$X$^-$. The organometallic tetrayne **4** (0.54 mmol) was reacted with 1 equiv of PdCl$_2$(PBu$^n_3$)$_2$ and a catalytic amount (1% mol equiv) of CuI, with diethylamine used as solvent. The dark orange oligomer **7** (^{31}P NMR (δ, ppm) 11.38 (s, PBu$_3$); ^{13}C NMR (δ, ppm) 115.19 (t, Pd—$C{\equiv}$C, $^2J_{PC}$ = 16.71 Hz), 110.74 (s, Pd—C$\equiv C$), 87.95 and 86.76 (s, $C{\equiv}C$C$_6$H$_4$-C$\equiv$C—Pd)) was obtained in 97% yield (GPC measurements: M_w = 21 400, P_w = 23; M_n = 11 400, I_p = 1.88) (Scheme 1). The use of the PBu$^n_3$ ligand was selected to increase the solubility of the oligomers, with respect to that of **4**, that is required for purification and NMR studies. The formation of oligomer is observed by the disappearance of the C$\equiv$CH ends in IR and NMR spectra and by ^{31}P spectroscopy. Under analogous conditions complex **4** (0.87 mmol) reacts with 1 equiv of *trans,trans*-Ni(C$\equiv$CH)$_2$(PBu$^n_3$)$_2$, as NiCl$_2$(PBu$^n_3$)$_2$ reacts with diethylamine, and the dark red oligomer **8** was isolated in 91% yield (^{31}P NMR (δ, ppm) 14.61 (s, PBu$_3$); ^{13}C NMR (δ, ppm) 119.70 (s, Ni—C$\equiv C$), 116.66 (t, Ni—$C{\equiv}$C, $^2J_{PC}$ = 40.59 Hz), 87.91 and 86.80 (s, $C{\equiv}C$C$_6$H$_4$C$\equiv$C—Ni)) (GPC measurements: M_w = 26 100, P_w = 29; M_n = 11 600, I_p = 2.25) (Scheme 1). Under similar catalytic conditions the reaction of the monomer **6** (0.18 mmol) with PdCl$_2$(PBu$^n_3$)$_2$ led to the yellow heterobimetallic oligomer **9** in 84% yield (^{13}C{^{1}H} NMR (δ, ppm) 136.92 (quint, Ru—C, $^2J_{PC}$ = 9.76 Hz) (GPC measurements: M_w = 14 800, P_w = 10; M_n = 7800, I_p = 1.90) (Scheme 2). The ^{31}P NMR of oligomer **9** shows two singlets (δ, ppm) in particular at 54.18 (PPh$_2$) and 11.59 (PBu$^n_3$) and the absence of its organometallic components **6** and PdCl$_2$(PBu$^n_3$)$_2$.

These mixed-metal oligomers correspond to two classes of macromolecules, one with rigid rods in a *zigzag* form due to the rotation of the cyclopentadienyl–iron bond (**7**, **8**) and the other with a linear *unidimensional* arrangement (**9**).

These results show that production of organometallic monomers containing C$\equiv$CH ends *via* a protection/deprotection method represents a convenient approach to build mixed-metal oligomers.

Supporting Information Available: Text giving synthetic procedures and spectroscopic data for compounds **3**–**9** and details of the molecular weight determination (4 pages). Ordering information is given on any current masthead page.

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