Use of Palladium-Catalyzed Coupling Reactions in the Synthesis of Heterobimetallic Complexes. Preparation of Bis(cyclopentadienyl) Complexes Linked by a (*Z*)-1,3-Enyne Bridge[†]

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Summary: Deprotonation of (η^5-HC≡CC$_5$H$_4$)ML$_n$ (**1**, ML$_n$ = Fe(CO)$_2$CH$_3$; **2**, ML$_n$ = Mn(CO)$_3$; **3**, ML$_n$ = W(CO)$_3$CH$_3$) followed by treatment with *N*-iodosuccinimide (NIS) or ICH$_2$CH$_2$I yielded the corresponding (η^5-IC≡CC$_5$H$_4$)ML$_n$ complex (**4**–**6**). In the case of the iron (**1**) and manganese (**2**) derivatives, KOH in CH$_3$OH is sufficient to remove the acetylenic proton, while in the case of the tungsten compound (**3**) *sec*-BuLi in THF is necessary to achieve the same result. Treatment of the alkynyl iodides **4**–**6** with a large excess of diimide led to the formation of the corresponding (*Z*)-vinyl iodides (**7**–**9**). Palladium-catalyzed coupling reactions of these (*Z*)-[(1-iodovinyl)cyclopentadienyl]metal complexes and the [((trimethylstannyl)ethynyl)cyclopentadienyl]metal complexes [η^5-(CH$_3$)$_3$SnC≡CC$_5$H$_4$]M′L$_m$ (**10**, M′L$_m$ = Fe(CO)$_2$CH$_3$; **11**, M′L$_m$ = Mn(CO)$_3$; **12**, M′L$_m$ = W(CO)$_3$CH$_3$; **13**, M′L$_m$ = Re(CO)$_3$) afforded the corresponding heterobimetallic bis(cyclopentadienyl) (*Z*)-enynes of general formula L$_n$M(η^5-C$_5$H$_4$)CH=CHC≡C(η^5-C$_5$H$_4$)M′L$_m$ (**14**–**21**) in good yields. The reaction takes place at room temperature in dimethylformamide in the presence of 5% bis(acetonitrile)dichloropalladium(II) catalyst.

The synthesis of polymetallic complexes has received overwhelming attention in recent years.[1] Much of the impetus for this interest came from the expectation that polynuclear complexes might perform a unique role in catalytic applications by the synergic effect of the different metal centers.[2–6]

As part of our studies on the preparation of new polymetallic complexes, we have recently described the synthesis of a variety of bimetallic complexes in which a bis(cyclopentadienyl)acetylene ligand was used to link two metal centers in a single frame.[7,8] These bimetallic complexes are easily accessible by a new synthetic route involving the palladium-catalyzed coupling reaction of the corresponding (η^5-iodocyclopentadienyl)- and [η^5-((trialkylstannyl)ethynyl)cyclopentadienyl]metal complexes. Moreover, the acetylenic bridge used to connect the two cyclopentadienyl rings can be the site for further elaboration of those structures by introduction of metal fragments such as Co$_2$(CO)$_8$ or any of the numerous organometallic species prone to attack a carbon–carbon triple bond. The X-ray structural determinations performed on those complexes as well as on related compounds[9] showed that the two metal centers are arranged in a "transoid" fashion with respect to the ligand plane. This configuration, as well as the large interatomic distance, makes the desired interaction between the two metal centers unlikely, even if a rotation around the bridging linkage were possible in solution.

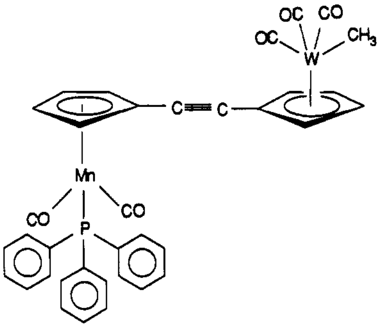

Figure 1. Transoid conformation of bis(cyclopentadienyl)acetylene framed complexes, as determined by X-ray analysis.[8,9]

The utility of the palladium-catalyzed coupling reaction in the formation of carbon–carbon bonds with a large variety of organic functionalities is well documented.[10] Our attention is focused on the application of this synthetic route to prepare new bimetallic complexes, in which the linkage between the cyclopentadienyl rings could bring the two metal units into close proximity, for potential bimetallic catalysis.

To pursue the goal of building a complex in which the metal units can stay in close proximity, we need to build a bidentate ligand that offers a greater flexibility than that of the simple bis(cyclopentadienyl)acetylene frame (Figure 1).

There are a number of reasons[11–13] it is preferable in building a polymetallic structure to have the metal centers complexed with cyclopentadienyl moieties, among which are the strong ligand ability of Cp toward transition metals and the consequent ability of maintaining a stable framework under operating conditions. Moreover, the wide variety of metals that the cyclopentadienyl ring can complex offers a great possibility of combination in the synthesis of heteropolymetallic species.

[†] Dedicated to the memory of Professor John K. Stille.

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With respect to the bis(cyclopentadienyl)acetylene structure shown in Figure 1, we need to bend the linkage between the two cyclopentadienyl rings. This has been achieved by linking a (*Z*)-vinyl group next to the acetylenic unit in order to have a (*Z*)-enyne bridge connecting the two rings. This synthetic route has been accomplished by a simple modification of the method previously used to prepare bis(cyclopentadienyl)acetylene complexes like that shown in Figure 1. Starting from the η^5-ethynylcyclopentadienyl derivatives (η^5-$HC{\equiv}CC_5H_4$)ML_n (M = Fe, Mn, W), prepared as previously reported,[8] the acetylenic proton was removed and substituted with iodine; then the acetylenic iodide was transformed into the (*Z*)-vinyl iodide (η^5-$ICH{=}CHC_5H_4$)ML_n by reduction with diimide. On the other hand, the ethynyl derivatives (η^5-$HC{\equiv}CC_5H_4$)$M'L_m$ (M' = Fe, Mn, Re, W) were reacted with $(CH_3CH_2)_2NSn(CH_3)_3$ to form the corresponding (trimethylstannyl)ethynyl partner [η^5-$(CH_3)_3SnC{\equiv}CC_5H_4$]$M'L_m$ for the palladium-catalyzed coupling reaction.

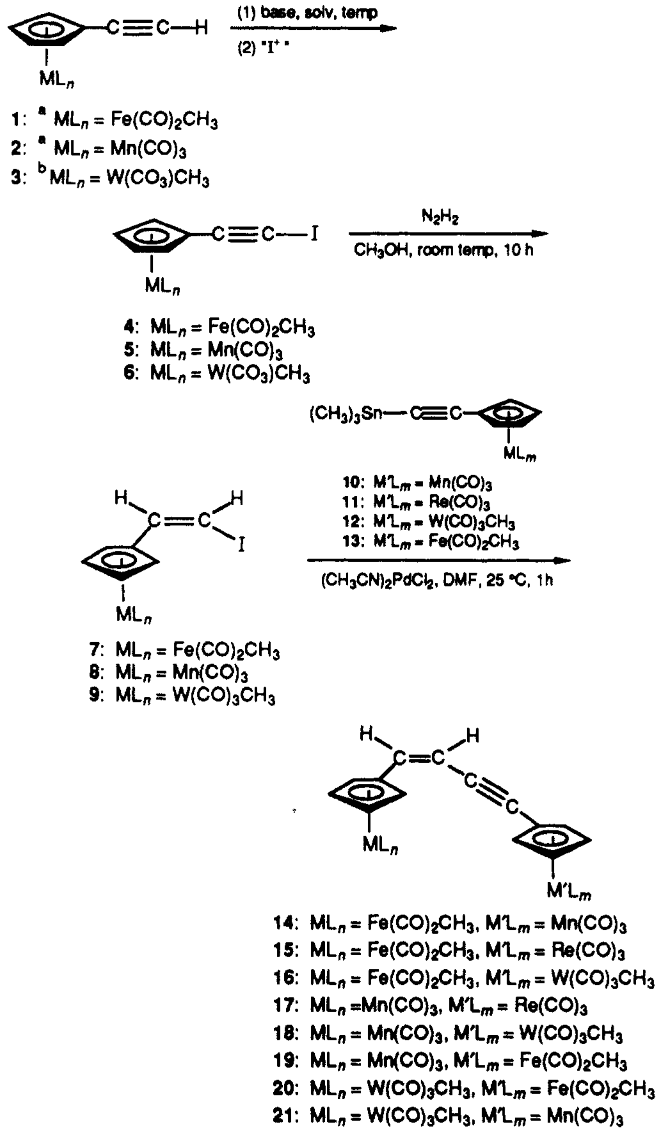
Results and Discussion

Synthesis of (η^5-$IC{\equiv}CC_5H_4$)ML_n (4–6). The replacement of the alkyne proton with iodine in substrates 1–3 has been accomplished by a modification of the reported procedure.[14] In our preparation, *N*-iodosuccinimide (NIS) or 1,2-diiodoethane (ICH_2CH_2I) was used instead of iodine, in order to avoid the undesired attack of the halogen atom at the methyl group on the metal. Thus, the reaction of (η^5-$HC{\equiv}CC_5H_4$)$Fe(CO)_2CH_3$ (1) and (η^5-$HC{\equiv}CC_5H_4$)$Mn(CO)_3$ (2) with 2.5 equiv of KOH in CH_3OH led, upon stirring at 0 °C for 30 min and subsequent treatment with NIS, to the corresponding alkynyl iodides (η^5-$IC{\equiv}CC_5H_4$)$Fe(CO)_2CH_3$ (4) and (η^5-$IC{\equiv}CC_5H_4$)$Mn(CO)_3$ (5). Under the same reaction conditions, the tungsten analogue (η^5-$HC{\equiv}CC_5H_4$)$W(CO)_3CH_3$ (3) was recovered unreacted. However, reaction occurred with *sec*-BuLi in THF at −78 °C and subsequent quenching of the anion with 1,2-diiodoethane. Yields of products 4–6 were nearly quantitative (Scheme I).

Reaction of Alkynyl Iodides (4–6) with Diimide. Formation of (*Z*)-Vinyl Iodides (7–9). Stereochemically pure (*Z*)-vinyl iodides can be obtained by the diimide reduction of acetylenic iodides.[15] Complexes 4–6, treated with a large excess (30/1) of diimide, gave the corresponding reduced products in good yields. Diimide was generated in situ by slow addition of a solution of acetic acid in methanol to a solution of the metal complex and potassium azodicarboxylate. The large excess of diimide is necessary in order to obtain complete reduction of the alkyne. In a preliminary run, even a 20-fold excess of diimide left some unreacted product. On the other hand, complete conversion causes unavoidable formation of some overreduced product. However, the amount of the overreduced product was very limited (less than 5%) and could be detected only by ^{1}H NMR spectroscopy.

Coupling Reactions. The (*Z*)-vinyl iodides (η^5-$ICH{=}CHC_5H_4$)ML_n (7–9) and the (trimethylstannyl)ethynyl derivatives [η^5-$(CH_3)_3SnC{\equiv}CC_5H_4$]$M'L_m$ (10–13) form a fortunate combination of substrates for palladium-catalyzed coupling reactions being respectively the most reactive electrophiles and stannanes that can be used in such synthetic routes.[10] The reactions take place in the presence of 5% bis(acetonitrile)dichloropalladium(II) at room temperature in *N,N*-dimethylformamide (DMF), to give high yields of products. In all cases the reaction is completed within 1 h. The crude reaction mixture was extracted with H_2O/Et_2O to get rid of DMF and the water-soluble byproduct $(CH_3)_3SnI$. The ^{1}H NMR spectrum of the crude reaction mixture shows complete conversion of the starting materials. Only the signal due to the reaction product appears in the spectra. However, when the reaction mixture was chromatographed on silica gel (flash) with hexane/CH_2Cl_2 as eluent, the product was eluted as a yellow-red band, but evaporation of the solvent from the eluent left, in all cases, a viscous oil and isolation of pure product, free of solvent, was difficult. Moreover, the coupled products are not stable enough, even when stored in the dark at low temperature, such that satisfactory elemental analyses can be obtained. Although yields appear to be quantitative on the basis of the NMR analysis, some decomposition occurs during the chromatography and the yields of the isolated compounds drop dramatically to 40–80%. All the complexes prepared throughout the series 14–21 are viscous oils whose colors vary from orange to red. This characteristic is completely different from that observed in the preparation of the corresponding complexes with two cyclopentadienyl rings linked by a simple acetylenic bridge. In fact, the latter compounds were all

Scheme I[a]



[a] base = KOH, solv = CH_3OH, temp = 0 °C, "I^+" = NIS. [b] base = *sec*-BuLi, solv = THF, temp = −78 °C, "I^+" = ICH_2CH_2I.

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high-melting solids.[8] Many attempts were made to grow X-ray-quality crystals of compounds **14–21**, in order to determine the molecular structure of one member of the series, but even at low temperature, with use of various combinations of solvents and techniques, only low-melting amorphous materials were recovered. However, the disappointing reluctance of these compounds to give crystalline material could be interpreted as an increased degree of freedom that the enyne linkage between the two Cp rings allows in structures **14–21**. It seems reasonable to think that rotation of the cyclopentadienyls is allowed to some extent even if the conjugation of the two cyclopentadienyls through the enyne linkage would keep the ligand geometry in a planar array. In fact, as reported in the X-ray structure for the related compound $CH_3(CO)_3W(\eta^5\text{-}C_5H_4)C{\equiv}C(\eta^5\text{-}C_5H_4)Mn(CO)_2P(C_6H_5)_3$[8] (Figure 1), the simple acetylenic linkage between the two Cp rings is already unable to maintain the coplanarity (that would be expected because of the conjugation), so that an angle of 15.6° was observed. Moreover, the enyne bridge should allow a certain degree of flexibility and consequently an increased difficulty for regular packing in a crystalline structure.

Some interesting spectroscopic features are shown by these compounds. The IR absorptions do not change significantly for the single monomers as one goes from compounds **1–3** throughout their transformation to compounds **4–6** and **7–9**. IR spectra of complexes **14–21** are merely the sum of the bands of the single components. However, ^1H NMR spectra show a significant change when the coupling reaction takes place. Compounds **7–9** exhibit, for the vinylic protons, two doublets centered at about 6.9 and 6.5 ppm, with a coupling constant of ca. 8.6 Hz. In the coupled products **14–21**, these resonances are shifted upfield about 0.65 and 0.80 ppm, respectively, with a new coupling constant in the range 11–12 Hz. This significative variation is consistent throughout all the complexes prepared. The other resonances (cyclopentadienyl protons and methyl groups) are not significantly affected in their chemical shifts by the coupling reaction. This marked variation could be used as a diagnostic tool to follow the completeness of the reaction. The same trend is observed in the ^{13}C NMR spectra through the series **14–21** with respect to their vinylic precursors **7–9**. A significant variation in the chemical shift of one of the vinylic carbons is observed. The resonance, probably due to the carbon bearing the iodine, moves from 79–81 to 107–108 ppm, while the other resonances are not substantially affected.

Experimental Section

All manipulations were carried out under a protective atmosphere of argon (deoxygenated with copper-based BTS catalyst (Fluka) and dried with 4-Å molecular sieves) in carefully dried equipment. Conventional vacuum-line and/or Schlenk-tube techniques were used. Liquids were transferred by syringe or cannula. Infrared spectra were recorded on a Nicolet FT 510 instrument in the solvent subtraction mode, using 0.1-mm NaCl cells. ^1H NMR spectra and the broad-band proton-decoupled ^{13}C NMR spectra were recorded in the Fourier transform mode on a Bruker WP-80 spectrometer and a Varian XL-300 spectrometer. The NMR chemical shifts are reported in parts per million vs Me_4Si, by assigning the ^1H impurity in the solvent ($CDCl_3$) at 7.24 ppm. The ^{13}C spectra chemical shifts are reported against the ^{13}C triplet ($CDCl_3$) at 77.00 ppm. High-resolution mass spectra (HRMS) were obtained on a Kratos M80 instrument. $(CH_3CN)_2PdCl_2$,[16] $(\eta^5\text{-}HC{\equiv}CC_5H_4)ML_n$ (M = Fe, Mn, W),[8] and $[\eta^5\text{-}(CH_3)_3SnC{\equiv}CC_5H_4]M'L_m$ (M′ = Fe, Mn, Re, W)[8] were prepared according to the literature procedures.

$(\eta^5\text{-}IC{\equiv}CC_5H_4)Fe(CO)_2CH_3$ (4). $(\eta^5\text{-}HC{\equiv}CC_5H_4)Fe(CO)_2CH_3$ (**1**; 1.56 g, 7.2 mmol) was dissolved under argon in 20 mL of methanol (dry, distilled from Mg/I_2), and was brought to 0 °C. Solid KOH (1.0 g, 18 mmol) was added and the stirring continued at low temperature for 20 min. Then 1.94 g (8.6 mmol) of solid NIS was added and the stirring continued at 0 °C for 15 min. The cold bath was removed and the flask warmed to room temperature for an additional 20 min. Then 200 mL of Et_2O was added and the mixture extracted three times with brine. The organic layer was separated, dried over $MgSO_4$, filtered, and evaporated. The product (2.4 g, 97%) was isolated as a brown oil. ^1H NMR ($CDCl_3$): δ 4.88 (t, 2 H, J = 2.05 Hz), 4.69 (t, 2 H, J = 2.05 Hz), 0.32 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 216.49, 89.76, 86.90, 84.96, 84.24, 82.93, −18.85. IR (CCl_4): 2016.2 vs, 1963.2 vs cm^{-1}. HRMS (m/e): calcd for $C_{10}H_7O_2FeI$, 341.8841; found, 341.8856.

$(\eta^5\text{-}IC{\equiv}CC_5H_4)Mn(CO)_3$ (5). As described above, this compound was prepared from 0.9 g (4.0 mmol) of $(\eta^5\text{-}HC{\equiv}CC_5H_4)Mn(CO)_3$ (**2**), 0.6 g (10 mmol) of KOH, and 1.4 g (6.0 mmol) of NIS. The product was recovered quantitatively as a red oil. IR (CCl_4): 2010.0 vs, 1935.0 vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.99 (t, 2 H, J = 2.1 Hz), 4.64 (t, 2 H, J = 2.10 Hz). ^{13}C NMR ($CDCl_3$): δ 223.83, 86.99, 85.77, 82.71, 82.01, 81.65. HRMS (m/e): calcd for $C_{10}H_4O_3IMn$, 353.8587; found, 353.8591.

$(\eta^5\text{-}IC{\equiv}CC_5H_4)W(CO)_3CH_3$ (6). $(\eta^5\text{-}HC{\equiv}CC_5H_4)W(CO)_3CH_3$ (**3**; 1.4 g, 3.7 mmol) was dissolved under argon in 100 mL of THF and cooled to −78 °C. *sec*-BuLi (3.1 mL, 3.7 mmol; 1.23 M solution in hexane) was added by syringe and the mixture stirred for 10 min at low temperature. Then 1.1 g (3.7 mmol) of 1,2-diiodoethane, dissolved in 20 mL of THF, was added to the flask and the cold bath removed. After it was warmed to room temperature, the solution was concentrated and filtered through a pad of alumina. Evaporation of the solvent gave the pure product (2.5 g, 93%). IR (CCl_4): 2021.0 vs, 1932.0 vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.50 (t, 2 H, J = 2.21 Hz), 5.24 (t, 2 H, J = 2.21 Hz), 0.53 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 214.78, 110.50, 94.43, 89.19, 88.83, 85.02, −28.25. HRMS (m/e): calcd for $C_{11}H_7O_3IW$: 497.8930; found, 479.8962.

General Procedure for Reduction of 4–6 with Diimide. This reaction was carried out in an identical manner for all three compounds. As an example, the experimental procedure for **5** is reported. Potassium azodicarboxylate was prepared by adding 12.8 g (110.4 mmol) of azodicarbonamide to a mechanically stirred 40% aqueous potassium hydroxide solution (50 mL), cooled by an external acetone/ice bath at a rate such that the temperature of the reaction mixture did not exceed 10 °C (30 min). After the addition was complete, the mixture was stirred for an additional 60 min (below 0 °C) and then filtered and the residue washed with 100 mL of cold methanol.

The solid potassium salt was placed in a 250-mL flask with 50 mL of methanol, and 1.3 g (3.7 mmol) of the (η^5-ethynylcyclopentadienyl)manganese tricarbonyl complex **5** was added. The mixture was stirred while a solution of 10.6 mL of acetic acid in 50 mL of methanol was added dropwise. After 10 h the reaction mixture was transferred to a separatory funnel containing 500 mL of water and extracted with three 100-mL portions of pentane. The pentane fractions were combined, washed with two 200-mL portions of water, dried over $MgSO_4$, and filtered. Evaporation of the solvent gave a crude product that was purified by chromatographic separation over silica with hexane as eluent; 1.123 g (82%) of product was recovered as a brown oil.

$(\eta^5\text{-}ICH{=}CHC_5H_4)Fe(CO)_2CH_3$ (7): brown oil, (78%); IR (CCl_4) 2012.1 vs, 1958.0 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.85 (d, 1 H, J = 8.64 Hz), 6.50 (d, 1 H, J = 8.64 Hz), 5.31 (t, 2 H, J = 1.87 Hz), 4.80 (t, 2 H, J = 1.87 Hz), 0.19 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 216.52, 132.03, 86.56, 83.59, 79.53, 67.91, −20.97; HRMS (m/e) calcd for C_8H_9Fe ($M^+ - 2CO$) 287.9099, found 287.9097.

$(\eta^5\text{-}ICH{=}CHC_5H_4)Mn(CO)_3$ (8): brown oil (82%); IR (CCl_4) 2052.2 vs, 1943.2 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.89 (d, 1 H, J = 8.58 Hz), 6.45 (d, 1 H, J = 8.58 Hz), 5.38 (t, 2 H, J = 1.72 Hz), 4.76 (t, 2 H, J = 1.72 Hz); ^{13}C NMR ($CDCl_3$) δ 224.26, 131.58, 83.88, 82.61, 81.86, 79.85. HRMS (m/e) calcd for C_7H_6Mn (M^+-3CO) 271.8897, found 271.8904.

$(\eta^5\text{-}ICH{=}CHC_5H_4)W(CO)_3CH_3$ (9): brown oil (86%); IR (CCl_4) 2019.0 vs, 1929.0 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.91 (d, 1 H, J = 8.73 Hz), 6.50 (d, 1 H, J = 8.73 Hz), 5.92 (t, 2 H, J = 2.37

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Hz), 5.37 (t, 2 H, J = 2.37 Hz), 0.43 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 215.56, 130.94, 91.44, 89.74, 89.63, 80.61, −31.07. HRMS (m/e) calcd for $C_{11}H_9O_3IW$ 499.9087, found 499.9081.

$CH_3(CO)_2Fe(\eta^5\text{-}C_5H_4)CH{=}CHC{\equiv}C(\eta^5\text{-}C_5H_4)Mn(CO)_3$ (14). A dry 50-mL Schlenk tube was charged with 0.011 g (0.052 mmol) of $(CH_3CN)_2PdCl_2$ and flushed with argon. DMF (30 mL) was added, and the solution was degassed three times by evacuating to 10 mmHg and flushing with argon. [(Z)-η^5-(1-Iodoethenyl)-cyclopentadienyl]iron dicarbonyl methyl (0.301 g, 0.877 mmol) was added to the yellow solution, causing a darkening to occur. [η^5-((Trimethylstannyl)ethynyl)cyclopentadienyl]manganese tricarbonyl (0.411 g, 1.052 mmol) was added to this mixture, causing the reaction mixture to immediately become black. The reactants were then stirred at 22–25 °C overnight. After this time, the reaction mixture was added to 50 mL of ether and the solution transferred to a separatory funnel. The solution was washed with water (3 × 50 mL), and the aqueous phase was back-extracted with ether (2 × 50 mL). The combined ethereal extracts were dried over magnesium sulfate, filtered, and, after addition of 20 g of Celite, evaporated to dryness in vacuo. The residue, added to a 3 × 40 cm column of silica gel (Kieselgel; Merck) and eluted with a 10% mixture of CH_2Cl_2 in hexane, gave after evaporation of the solvent under vacuum 0.29 g (74%) of the product as an orange oil. IR (CCl_4): 2028.3 vs, 2011.0 vs, 1950.3 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.21 (d, 1 H, J = 11.56 Hz), 5.71 (d, 1 H, J = 11.56 Hz), 5.25 (t, 2 H, J = 2.21 Hz), 5.07 (t, 2 H, J = 2.19 Hz), 4.78 (t, 2 H, J = 2.21 Hz), 4.70 (t, 2 H, J = 2.19 Hz), 0.22 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 224.74, 217.24, 133.21, 107.93, 96.55, 88.20, 87.26, 86.98, 83.79, 82.07, 81.83, −21.07. HRMS (m/e): calcd for $C_{15}H_{13}FeMn$ ($M^+ - 5CO$), 303.9747; found, 303.9747.

$CH_3(CO)_2Fe(\eta^5\text{-}C_5H_4)CH{=}CHC{\equiv}C(\eta^5\text{-}C_5H_4)Re(CO)_3$ (15). This compound was prepared from 0.247 g (0.720 mmol) of [(Z)-η^5-(1-iodoethenyl)cyclopentadienyl]iron dicarbonyl methyl, 0.451 g (0.864 mmol) of [η^5-((trimethylstannyl)ethynyl)cyclopentadienyl]rhenium tricarbonyl, and 0.009 g (0.036 mmol) of $(CH_3CN)_2PdCl_2$ in 20 mL of DMF, with use of the method described for 14. After the workup 0.16 g (38%) of a red oil was recovered. IR (CCl_4): 2030.2 vs, 2011.1 vs, 1956.7 vs, 1940.5 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.24 (d, 1 H, J = 11.66 Hz), 5.72 (d, 1 H, J = 11.66 Hz), 5.68 (t, 2 H, J = 2.00 Hz), 5.29 (t, 2 H, J = 2.00 Hz), 5.21 (t, 2 H, J = 1.89 Hz), 4.80 (t, 2 H, J = 1.89 Hz), 0.22 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 216.71, 192.96, 133.59, 107.46, 96.20, 88.94, 87.77, 87.35, 83.90, 83.64, 83.53, −20.64. HRMS (m/e): calcd for $C_{20}H_{13}O_5FeRe$, 575.9642; found, 575.9651.

$CH_3(CO)_2Fe(\eta^5\text{-}C_5H_4)CH{=}CHC{\equiv}C(\eta^5\text{-}C_5H_4)W(CO)_3CH_3$ (16). This compound was prepared from 0.318 g (0.925 mmol) of [(Z)-η^5-(1-iodoethenyl)cyclopentadienyl]iron dicarbonyl methyl, 0.594 g (1.110 mmol) of [η^5-((trimethylstannyl)ethynyl)cyclopentadienyl]tungsten tricarbonyl methyl, and 0.014 g (0.055 mmol) of $(CH_3CN)_2PdCl_2$ in 30 mL of DMF, by the method described for 14. After the workup 0.21 g (39%) of a red oil was recovered. IR (CCl_4): 2020.1 vs, 2011.4 vs, 1957.8 vs, 1930.8 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.22 (d, 1 H, J = 12.19 Hz), 5.77 (d, 1 H, J = 12.19 Hz), 5.53 (t, 2 H, J = 2.33 Hz), 5.31 (t, 2 H, J = 2.33 Hz), 5.23 (t, 2 H, J = 1.90 Hz), 4.79 (t, 2 H, J = 1.90 Hz), 0.56 (s, 3 H), 0.22 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 217.14, 215.40, 133.46, 107.63, 96.46, 93.98, 92.28, 90.09, 88.96, 88.15, 87.31, 83.86, −20.96, −29.71. HRMS (m/e): calcd for $C_{17}H_{16}OFeW$ ($M^+ - 4CO$), 476.0039; found, 476.0080.

$(CO)_3Mn(\eta^5\text{-}C_5H_4)CH{=}CHC{\equiv}C(\eta^5\text{-}C_5H_4)Re(CO)_3$ (17). This compound was prepared from 0.560 g (1.57 mmol) of [(Z)-η^5-(1-iodoethenyl)cyclopentadienyl]manganese tricarbonyl, 0.987 g (1.89 mmol) of [η^5-((trimethylstannyl)ethynyl)cyclopentadienyl]rhenium tricarbonyl, and 0.024 g (0.094 mmol) of $(CH_3CN)_2PdCl_2$ in 30 mL of DMF, with use of the method described for 14. After the workup 0.88 g (96%) of a red oil was recovered. IR (CCl_4): 2030.0 vs, 2025.0 vs, 1942.0 vs cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 6.26 (d, 1 H, J = 11.59 Hz), 5.63 (d, 1 H, J = 11.59 Hz), 5.70 (t, 2 H, J = 2.21 Hz), 5.29 (t, 4 H, J = 2.21 Hz), 4.74 (t, 2 H, J = 2.21 Hz). ^{13}C NMR ($CDCl_3$) δ 225.05, 193.37, 133.40, 107.51, 95.78, 89.98, 89.14, 86.75, 84.64, 83.94, 83.72, 82.36. HRMS (m/e): calcd for $C_{20}H_{10}O_6MnRe$, 587.9387; found, 587.9398.

$(CO)_3Mn(\eta^5\text{-}C_5H_4)CH{=}CHC{\equiv}C(\eta^5\text{-}C_5H_4)W(CO)_3CH_3$ (18). This compound was prepared from 0.344 g (0.966 mmol) of [(Z)-η^5-(1-iodoethenyl)cyclopentadienyl]manganese tricarbonyl, 0.620 g (1.115 mmol) of [η^5-((trimethylstannyl)ethynyl)cyclopentadienyl]tungsten tricarbonyl methyl, and 0.014 g (0.057 mmol) of $(CH_3CN)_2PdCl_2$ in 30 mL of DMF by using the method described for 14. After the workup 0.31 g (54%) of an orange oil was recovered. IR (CCl_4): 2022.0 vs, 1935.8 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.26 (d, 1 H, J = 11.44 Hz), 5.67 (d, 1 H, J = 11.44 Hz), 5.54 (t, 2 H, J = 1.98 Hz), 5.32 (t, 4 H, J = 1.98 Hz), 4.74 (t, 2 H, J = 1.98 Hz), 0.56 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 224.45, 214.95, 132.85, 107.50, 95.99, 94.01, 91.87, 90.29, 88.24, 84.53, 82.31, 82.16, −29.45. HRMS (m/e): calcd for $C_{21}H_{13}O_6MnW$, 599.9581; found, 599.9593.

$(CO)_3Mn(\eta^5\text{-}C_5H_4)CH{=}CHC{\equiv}C(\eta^5\text{-}C_5H_4)Fe(CO)_2CH_3$ (19). This compound was prepared from 0.233 g (0.656 mmol) of [(Z)-η^5-(1-iodoethenyl)cyclopentadienyl]manganese tricarbonyl, 0.298 g (0.787 mmol) of [η^5-((trimethylstannyl)ethynyl)cyclopentadienyl]iron dicarbonyl methyl, and 0.010 g (0.039 mmol) of $(CH_3CN)_2PdCl_2$ in 10 mL of DMF by using the method described for 14. After the workup 0.12 g (41%) of a yellow-brown oil was recovered. IR (CCl_4): 2024.7 vs, 2014.8 vs, 1960.7 vs, 1944.7 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.24 (d, 1 H, J = 11.73 Hz), 5.64 (d, 1 H, J = 11.73 Hz), 5.36 (t, 2 H, J = 2.08 Hz), 4.96 (t, 2 H, J = 2.20 Hz), 4.76 (t, 2 H, J = 2.08 Hz), 4.73 (t, 2 H, J = 2.20 Hz), 0.36 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 224.60, 216.20, 132.14, 108.17, 96.38, 91.03, 90.11, 86.74, 84.95, 83.29, 82.56, 82.19, −19.67. HRMS (m/e): calcd for $C_{20}H_{13}O_5FeMn$, 443.9492; found, 443.9481.

$CH_3(CO)_3W(\eta^5\text{-}C_5H_4)CH{=}CHC{\equiv}C(\eta^5\text{-}C_5H_4)Fe(CO)_2CH_3$ (20). This compound was prepared from 0.278 g (0.557 mmol) of [(Z)-η^5-(1-iodoethenyl)cyclopentadienyl]tungsten tricarbonyl methyl, 0.253 g (0.668 mmol) of [η^5-((trimethylstannyl)-ethynyl)cyclopentadienyl]iron dicarbonyl methyl, and 0.008 g (0.033 mmol) of $(CH_3CN)_2PdCl_2$ in 20 mL of DMF by using the method described for 14. After the workup 0.17 g (52%) of a red oil was recovered. IR (CCl_4): 2016.7 vs, 1961.6 vs, 1929.0 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.25 (d, 1 H, J = 11.56 Hz), 5.85 (t, 2 H, J = 2.27 Hz), 5.72 (d, 1 H, J = 11.56 Hz), 5.34 (t, 2 H, J = 2.27 Hz), 4.96 (t, 2 H, J = 2.13 Hz), 4.77 (t, 2 H, J = 2.13 Hz), 0.45 (s, 3 H), 0.36 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 228.67, 216.15, 130.93, 108.80, 94.53, 91.46, 90.25, 90.05, 89.90, 89.00, 86.61, 83.34, −19.63, −30.25. HRMS (m/e): calcd for $C_{21}H_{16}O_5FeW$, 587.9836; found, 587.9857.

$CH_3(CO)_3W(\eta^5\text{-}C_5H_4)CH{=}CHC{\equiv}C(\eta^5\text{-}C_5H_4)Mn(CO)_3$ (21). This compound was prepared from 0.223 g (0.447 mmol) of [(Z)-η^5-(1-iodoethenyl)cyclopentadienyl]tungsten tricarbonyl methyl, 0.209 g (0.536 mmol) of [η^5-((trimethylstannyl)-ethynyl)cyclopentadienyl]manganese tricarbonyl, and 0.005 g (0.022 mmol) of $(CH_3CN)_2PdCl_2$ in 10 mL of DMF by using the method described for 14. After the workup 0.15 g (58%) of a brown oil was recovered. IR (CCl_4): 2029.0 vs, 2018.4 vs, 1948.9 vs, 1930.3 vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.25 (d, 1 H, J = 11.39 Hz), 5.82 (t, 2 H, J = 2.19 Hz), 5.70 (d, 1 H, J = 11.39 Hz), 5.34 (t, 2 H, J = 2.19 Hz), 5.08 (t, 2 H, J = 1.97 Hz), 4.71 (t, 2 H, J = 1.97 Hz), 0.45 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 224.44, 216.35, 131.57, 108.50, 94.55, 91.43, 90.06, 89.14, 87.49, 86.25, 82.08, 81.94, −30.84. HRMS (m/e): calcd for $C_{21}H_{13}O_6MnW$, 599.9581; found, 599.9576.

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