Polynuclear Complexes with Propynylidene C_3-Bridges: General Synthetic Route to Bis-, Tris-, and Tetrakis(ethynylcarbene) Complexes☆

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The sequential reaction of two equivalents of the dimethylamino(ethynyl)carbene complexes $[(CO)_5M{=}C(NMe_2)C{\equiv}CH]$ [M = W (**1a**), Cr (**1b**)] with two equivalents of *n*BuLi and one equivalent of a transition metal dichloride, $[Cl_2M'(L_n)]$, affords trinuclear biscarbene complexes of the type $[(CO)_5M{=}C(NMe_2)C{\equiv}C{-}M'(L_n){-}C{\equiv}CC(NMe)_2{=}M(CO)_5]$ $[M'(L_n)$ = $Ni(PEt_3)_2$ (**2a**, **b**), $Pd(PEt_3)_2$ (**3a**, **b**), $Pt(PEt_3)_2$ (**4a**, **b**), $Fe(dmpe)_2$ (**6a**), Hg (**8a**), $Ti(\eta^5\text{-}C_5H_5)_2$ (**9a**, **b**)] [dmpe = 1,2-bis(dimethylphosphino)ethane]. Treatment of **1a** with equimolar amounts of first *n*BuLi and then $[Cl_2M'(L_n)]$ results in the formation of the monosubstitution products $[(CO)_5W{=}C(NMe_2)C{\equiv}CM'(L_n)]$ $[M'(L_n)$ = *trans*-$Pd(PEt_3)_2Cl$ (**5a**), *trans*-$Fe(dmpe)_2Cl$ (**7a**)]. Additionally, the synthesis of the heterobimetallic ethynylcarbene complex $[(CO)_5W{=}C(NMe_2)C{\equiv}CPd(PEt_3)_2C{\equiv}CH]$ (**10a**), starting from **1a** and $[ClPd(PEt_3)_2C{\equiv}CH]$, is described. When three equivalents of **1a** are treated, first with three equivalents of *n*BuLi and then with one equivalent of the trihalides PCl_3 or BBr_3, the novel tris(ethynylcarbene) complexes $[\{(CO)_5W{=}C(NMe_2)C{\equiv}C\}_3E]$ [E = B (**11a**), P (**12a**)] are obtained. The reaction of four equivalents of **1a**, **b** with four equivalents of *n*BuLi, followed by addition of one equivalent of a group 14 tetrachloride $[M'Cl_4]$, yields the novel tetrakis(ethynylcarbene) complexes $[\{(CO)_5M{=}C(NMe_2)C{\equiv}C\}_4M']$ [M′ = Si (**13a**, **b**), Ge (**14a**), Sn (**15a**, **b**)]. The complexes **8a**, **9a**, **12a**, and **15a** were characterized by X-ray structural analyses. All spectroscopic and structural data suggest that the carbene fragments and the central transition metal or heteroatom in these new bis-, tris-, and tetrakis(ethynylcarbene) complexes interact only weakly.

Introduction

Polynuclear transition metal complexes with π-conjugated carbon bridges have recently attracted considerable interest due to their potentially useful chemical and physical properties. An application as materials for nonlinear optics has been proposed[1]. In addition, π systems, such as highly ethynylated organic and organometallic compounds, have been intensively studied since they represent viable monomers for the synthesis of high carbon polymers. Transition metal σ-acetylide complexes[2] and ethynyl-substituted half sandwich complexes can be considered as building blocks in the synthesis of linear[3], star-shaped[3d][4], and spherical[5] structures.

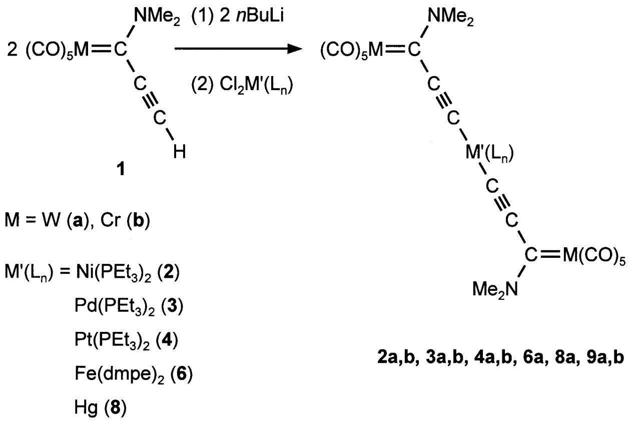
A wide range of π-conjugated acetylide transition metal complexes of the type $[L_nM{-}(C{\equiv}C)_x{-}M'L'_{n'}]$ have already been reported[1a]. Examples for conjugated bis(Fischer carbene)complexes of the type $[L_nMC(YR)\mathbf{C}_c(RY)CML_n]$ (with $\mathbf{C}_c$ = conjugated carbon bridge, Y = O, NR) are also known. Symmetrical complexes containing phenyl[6][7], biphenyl[8], binaphthyl[7], anthracene[9], 1,6-methano[10]annulene-2,7-diyl[10], alkenyl,[11] or ammonium pentadienide[12] bridges are readily accessible. By contrast, apart from our results on the synthesis of the C_4HgC_4-bridged complex $[(CO)_5W{=}C(NMe_2)C{\equiv}CC{\equiv}CHgC{\equiv}CC{\equiv}CC(NMe_2){=}W(CO)_5]$[13], examples of π-conjugated metal-bridged trinuclear biscarbene complexes are unknown[14]. Nevertheless, all these systems may represent suitable substructures for the construction of two- and three-dimensional networks.

Previously, we reported on the efficient preparation of bimetallic ethynylcarbene complexes by nucleophilic substitution of a lithiated ethynyl- or butadiynylcarbene complex for the halide X in metal monohalides $[XM'(L'_m)]$[13][15]. In this paper we report on a general synthetic route to a wide range of π-conjugated metal-bridged bis-, tris-, and tetrakis(Fischer carbene) complexes. These carbene complexes can be considered as a new type of monomeric polyacetylenic organometallic building blocks for the synthesis of two and three dimensional structures.

Results and Discussion

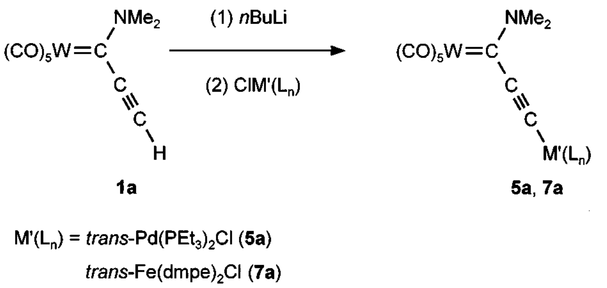
Extension of the concept of coupling a L_nMC_3 with a $M'L_m$ fragment to the treatment of the dimethylamino(ethynyl)carbene complexes of tungsten and chromium with different metal dihalides afforded metal-bridged biscarbene complexes of the general type $[(CO)_5M{=}C(NMe_2)C{\equiv}C{-}M'(L_m){-}C{\equiv}CC(NMe_2){=}M(CO)_5]$. The dimethylamino(trimethylsilylethynyl)carbene complexes $[(CO)_5M{=}C(NMe_2)C{\equiv}CSiMe_3]$ (M = W, Cr) proved to be suitable precursors for the L_nMC_3 fragment. Desilylation with KF/THF/MeOH[15], followed by deprotonation with *n*BuLi, gave the lithiated acetylide $[(CO)_5M{=}C(NMe_2)C{\equiv}CLi]$ (M = W, Cr). Treatment of two equivalents of this tungstate (or chromate) in situ with one equivalent of the metal dichloride $[Cl_2M(PEt_3)_2]$ (M = Ni, Pd, Pt) resulted in formation of the pale yellow *trans*-bis(ethynylcarbene) complexes **2**−**4** in yields, after chromatography, of 66−72% (Scheme 1).

Scheme 1



As expected, the reaction of equimolar amounts of the lithiated complex $[(CO)_5W{=}C(NMe_2)C{\equiv}CLi]$ and a metal dichloride under the same conditions led to the formation of a monosubstituted product. Thus, when **1a** was treated at −80°C, first with *n*BuLi and then with the equimolar amount of $[Cl_2Pd(PEt_3)_2]$, chromatographic work up of the reaction mixture afforded the complex **5a** in a yield of 61% (Scheme 2).

Scheme 2



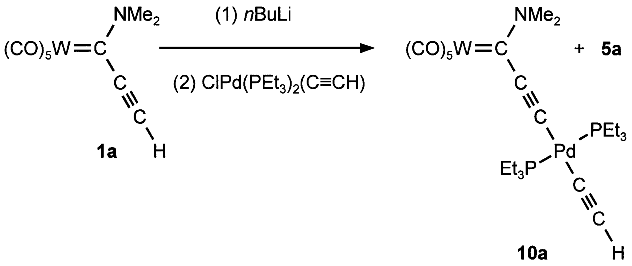
Analogous reaction sequences were carried out with the iron dichloride $[Cl_2Fe(dmpe)_2]$ [dmpe = 1, 2-bis(dimethylphosphino)ethane]. Addition of an equimolar amount of *n*BuLi to two equivalents of **1a**, followed by addition of one equivalent of the metal dichloride, gave the linear *trans*-substituted trinuclear complex **6a** in a yield of 35% (Scheme 1). The reaction of equimolar amounts of the educt complexes resulted in the formation of the bimetallic ethynylcarbene complex **7a** in a yield of 29% (Scheme 2).

Similar to **2**−**4**, and **6**, treatment of two equivalents of deprotonated ethynylcarbene complex **1a** and one equivalent of the dichloride $HgCl_2$ resulted in the formation of a linear biscarbene complex (Scheme 1). Chromatographic work up of the reaction mixture afforded compound **8a** in a yield of 57%. This *trans*-coordinated complex represents the only trinuclear complex without any coligands at the central metal in this series.

A tetrahedrally coordinated trinuclear biscarbene complex was obtained, when two equivalents of the lithiated complexes **1a**, **b** were treated with one equivalent of the dichloride $[Cl_2Ti(\eta^5\text{-}C_5H_5)_2]$ (Scheme 1). The red biscarbene complexes **9a**, **b** were obtained in yields of 67% (**9a**) and 68% (**9b**), respectively. Tweezer compounds such as the bisalkynyl substituted titanocene complexes of the type $[(\eta^5\text{-}C_5H_4R)_2Ti(C{\equiv}CR')_2]$ are well known[16][17][18]. The formation of monoalkynyl substituted titanocenes $[(\eta^5\text{-}C_5H_4R)_2TiCl(C{\equiv}CR')]$ by reaction of equimolar amounts of an acetylide and a metal dihalide could also be observed[16]. Efforts to prepare an analogous monosubstituted ethynylcarbene complex $[(CO)_5W{=}C(NMe_2)C{\equiv}CTiCl(\eta^5\text{-}C_5H_5)_2]$ starting from **1a** failed. Only a small amount of the disubstituted product **9a** was isolated.

Apart from **2**−**4**, and **8a** the synthesis of asymmetrically π-conjugated linear systems was intended. Treatment of the deprotonated complex **1a** with $[ClPd(PEt_3)_2C{\equiv}CH]$ afforded the light yellow ethynyl propynylidene palladium complex $[(CO)_5W{=}C(NMe_2)C{\equiv}CPd(PEt_3)_2C{\equiv}CH]$ **10a** in rather moderate yield (23%) (Scheme 3). The monosubstitution product **5a** was obtained as a by-product in a yield of 19%. Obviously, the ethynyl chloro palladium complex was contaminated with small amounts of $[Cl_2Pd(PEt_3)_2]$, which reacted with deprotonated **1a** to yield **5a**. Further investigations, in order to optimize the synthesis of **10a** and to apply this compound as starting material for polynuclear complexes with longer π-conjugated metal−carbon systems, are presently under way.

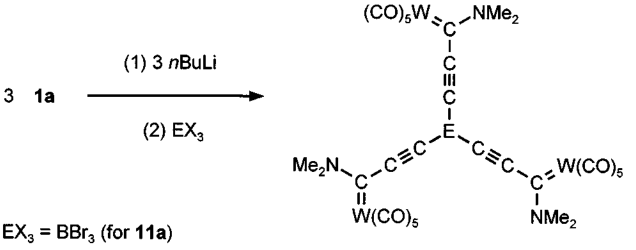
Scheme 3



The nucleophilic substitution of complexes **1a** and **1b** is not restricted to transition metal halides, but can also be applied to halides of main group elements. By the reaction of three equivalents of the deprotonated ethynylcarbene complex **1a** with one equivalent of either the group 13 trihalide BBr_3, or the group 15 trihalide PCl_3 tris(ethynylcarbene) complexes of the general type $[\{(CO)_5W{=}C(NMe)_2C{\equiv}C\}_3E]$ were obtained in good to high yield [E = B: 61% (**11a**), P: 81% (**12a**)] (Scheme 4).

Tetrahalides of the main group metals can also be employed for analogous nucleophilic substitution reactions with the lithiated complex **1**. When four equivalents of the deprotonated ethynylcarbene complex **1a** were treated with one equivalent of a group 14 tetrachloride $M'Cl_4$, pentanuclear tetrakiscarbene complexes $\{[(CO)_5W{=}C(NMe)_2C{\equiv}C]_4M'\}$ were obtained in good yield [M' = Si: 60% (**13a**), Ge: 59% (**14a**), Sn: 76% (**15a**)] (Scheme 5). In the case of silicium and tin the corresponding chromium

Scheme 4



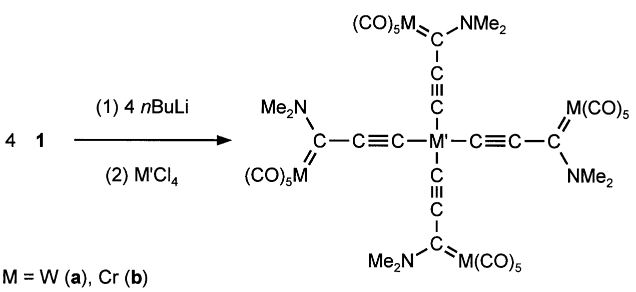
EX$_3$ = BBr$_3$ (for **11a**)
PCl$_3$ (for **12a**)

11a, 12a

complexes were prepared in a similar manner with yields of 54% (**13b**) and 71% (**15b**), respectively.

All complexes **13–15** are stable in the solid state and in solution, when carefully dried solvents are used. In the series Sn → Ge → Si the tin compounds are the most stable. By comparison, the M–C bond of the silicium and germanium derivatives is easily cleaved by hydrolysis or by contact with silica. Therefore, complexes **14a** and **15a**, **b** can only be filtered over cellite, whereas **14a**, **b** can be purified by column chromatography on silica.

Scheme 5



M = W (**a**), Cr (**b**)
M' = Si (**13**), Ge (**14**), Sn (**15**)

13a,b, 14a, 15a,b

All other new complexes are stable at room temp. Compounds **2–15** were characterized by spectroscopic means and elemental analyses. The positions of the ν(CO) absorptions of the pentacarbonyl metal moiety in complexes **2–4**, **8a**, and **9** are only slightly influenced by variation of the propynylidene metal substituent $M'(L_n)$. In contrast, the absorptions of the two iron-substituted complexes **6a** and **7a** are found at lower wavenumbers. The unsymmetrically substituted compounds **5a** and **10a** show absorptions similar to those of the *trans*-biscarbene complex **3a**. However, the A^1(*trans*) and the E absorptions of all complexes **2–10a** are at significantly smaller wavenumbers than those of the corresponding educt complexes **1**, indicating the π-basic properties of $M'(L_n)$ in $[(CO)_5M{=}C(NMe_2)C{\equiv}C{-}M'(L_n){-}C{\equiv}CC(NMe_2){=}M(CO)_5]$ or $[(CO)_5M{=}C(NMe_2)C{\equiv}CM'(L_n)]$, respectively. This tendency is less pronounced for the tris- and tetrakis(ethynylcarbene) complexes **11a**, **12a**, and **13–15**.

The two carbene fragments of the linear trinuclear biscarbene complexes **2–4**, **6a**, and **8a** can be regarded as π-conjugated. The ethynyl groups can mutually interact through metal d_{xy} and d_{yz} orbitals. For *trans*-coordinated square-planar dialkynyl complexes $[(Et_3P)_2M(C{\equiv}CR)_2]$ (M = Ni, Pd, Pt), showing the same D_{2h} symmetry, π-conjugation involving the metal d-orbitals has already been discussed[19].

The stretching frequencies of the carbon–carbon triple bonds in the complexes **2–4** are significantly smaller than those of the unsubstituted ethynylcarbene complexes **1** [$\tilde{\nu}(C{\equiv}C)$ = 2118 cm^{-1}]. This is commonly observed with σ-acetylenic transition metal complexes, and can be considered as evidence for the increase in polarity of the acetylenic bond upon coordination to the metal[17][20]. In the series **2** → **3** → **4** the ν(C≡C) absorptions shift to higher wavenumbers due to the increasing donating capacity of the $M'(PEt_3)_2$ moiety, and thus to the increasing polarity of the C≡C bond. For alkynyl complexes of group 10 metals an analogous order of ν(C≡C) frequencies has been noted[20]. In this case the M←CCR bond polarity, and not the M→CCR π-backbonding[20], was found to exert the dominating influence on the ν(C≡C) frequency.

For the two inequivalent *trans*-ethynyl moieties in **10a** only one ν(C≡C) absorption was observed [$\tilde{\nu}(C{\equiv}C)$ = 2036 cm^{-1}]. Compared to **3a** and **10a**, complex **5a** shows a ν(C≡C) absorption band at significantly higher energy [$\tilde{\nu}(C{\equiv}C)$ = 2032 cm^{-1} (**3a**), 2045 cm^{-1}(**5a**)]. The *trans*-position of the chloride ligand is known to cause a decrease in the polarity of the M–C≡ bond[21] thus leading to the observed shift of the ν(C≡C) absorption. The same tendency has already been observed for the disubstituted complex $[PhC{\equiv}CPd(PPh_3)_2C{\equiv}CPh]$ [$\tilde{\nu}(C{\equiv}C)$ = 2110 cm^{-1}][22] and the monosubstituted derivative $[ClPd(PPh_3)_2C{\equiv}CPh]$ [$\tilde{\nu}(C{\equiv}C)$ = 2125 cm^{-1}][23]. Compared to the phenyl substituted ethynyl complexes $[PhC{\equiv}CM(PEt_3)_2C{\equiv}CPh]$ (M = Ni, Pd, Pt)[22], $[PhC{\equiv}CFe(dmpe)_2C{\equiv}CPh]$[24] and $[ClFe(dmpe)_2C{\equiv}CPh]$[25] the ν(C≡C) band of complexes **2–4**, **6a**, and **7a** is at lower wavelength, indicating that the $(CO)_5M{=}C(NMe_2)$ fragment acts as a stronger donor than the phenyl group. The IR spectrum of **8a** shows no ν(C≡C) band although a ν(C≡C) absorption can be observed for the phenyl substituted complex $[Hg(C{\equiv}CPh)_2]$[26]. Similarly, but in contrast to $[(\eta^5\text{-}C_5H_4R)_2Ti(C{\equiv}CR')_2]$ (R' = alkyl, aryl, $SiMe_3$)[16c], no ν(C≡C) absorption was observed for the complexes **9**.

Complex **11a** shows a very weak ν(C≡C) absorption at $\tilde{\nu}$ = 2126 cm^{-1}. However, no ν(C≡C) absorption was observed for **12a**, in contrast to $P(C{\equiv}CR)_3$ with R = H, Me, or Ph[27][28][29]. The frequencies of the ν(C≡C) absorption of the tetrakiscarbene complexes **13–15** decrease in the series **13** → **14** → **15** [$\tilde{\nu}(C{\equiv}C)$ = 2132 cm^{-1} (**13a**, **14a**), 2118 cm^{-1} (**15a**)]. A similar tendency is observed for $[M'(C{\equiv}CH)_4]$ [$\tilde{\nu}(C{\equiv}C)$ = 2062 cm^{-1} (M' = Si, Ge), 2042 cm^{-1} (M' = Sn)][30], but the opposite trend is observed for the biscarbene complexes **2–4**.

The resonance of the carbene carbon atom in the ^{13}C-NMR spectra of the complexes **2–15** is at rather high field (δ = 238–250 for M = Cr and δ = 218–231 for M = W). This compares well with the shifts usually observed for simple aminocarbene complexes. As expected from the trend in the IR spectroscopic data of **1** and **2–9**, substitution of $M'(L_n)$ for H in compounds of the type $[(CO)_5M{=}C(NMe_2)C{\equiv}CR]$ [R = H, $M'(L_n)$] results in an upfield shift of the C(carbene) resonance. A similar trend is observed for the tris- and tetrakis(ethynylcarbene) complexes **11a**, **12a**, and **13−15**.

The ethynyl $^{13}C_{\alpha}$ and $^{13}C_{\beta}$ resonances of complexes **2−4** were unambiguously assigned on the basis of the coupling constants $J_{^{13}C,^{31}P}$ and in the case of **4** additionally on the basis of the coupling constants $J_{^{13}C,^{31}P}$. As a rule, the relationship $|^{2}J_{^{13}C,^{31}P}| > |^{3}J_{^{13}C,^{31}P}|$ was used in analogy to the assignment of the C_{α} and C_{β} resonances of the corresponding bisalkynyl complexes $[RC_{\beta}{\equiv}C_{\alpha}M(PEt_3)_2\text{-}C_{\alpha}{\equiv}C_{\beta}R]$[21].

The shielding of the C_{α} and the C_{β} atom increases with increasing radius of the central metal (Ni < Pd < Pt). This observation has already been made for alkyl- or aryl-substituted bisalkynyl complexes of these metals[21] and is consistent with the IR spectroscopic data of **2−4**.

The difference $\Delta = \delta(C_{\alpha})-\delta(C_{\beta})$ in the ethynyl resonances for **3** [Δ = 41.04 ppm (**3a**), 45.0 ppm (**3b**)] and **4** [Δ = 35.01 ppm (**4a**), 38.98 ppm (**4b**)] is much more pronounced than for the phenyl-substituted bisalkynyl complexes $[PhC{\equiv}CM(PEt_3)_2C{\equiv}CPh]$ [M = Pd: Δ = 0.3 ppm, δ = 111.7 (C_{α}), 111.4 (C_{β})[21]; M = Pt: Δ = −1.7 ppm, δ = 108.3 (C_{α}), 110.0 (C_{β})][31] which indicates an increased polarity of the C≡C bond in the biscarbene complexes **2−4** when compared to bisalkynyl complexes. This can be explained with the stronger π-basic capacity of the $(CO)_5M{=}C(NMe_2)$ fragment relative to the phenyl group.

As already discussed, the π-backbonding of the central metal to the acetylide ligand is more pronounced in the halide-substituted complex **5a** than in the biscarbene compounds **2−4**. This tendency is reflected in the highfield shift of the C_{α} and C_{β} resonance of **5a** [δ = 149.51 (C_{α}), 118.68 (C_{β})] when compared to **3a** [δ = 163.88 (C_{α}), 122.84 (C_{β})]. The same trend has been found in the ^{13}C- and ^{31}P-NMR spectra of comparable bisalkynyl complexes $[RC{\equiv}CM(PEt_3)_2C{\equiv}CR]$[21] and alkynyl complexes $[ClM(PEt_3)_2C{\equiv}CR]$[21].

Compared to **2a−4a**, the Fe(dmpe)$_2$-substituted complexes **6a** and **7a** show a significant lowfield shift of the ethynyl resonances. Therefore, the Fe(dmpe)$_2$ fragment seems to have a stronger π-backbonding capacity than the $M(PEt_3)_2$ fragment (M = Ni, Pd, Pt). In contrast to **3a** and **5a**, the substitution of $(CO)_5W{=}C(NMe)_2C{\equiv}C$ in **6a** for Cl in **7a** does not result in a significant shift of the ethynyl resonances [**6a**: δ = 195.33 (C_{α}), 135.10 (C_{β}); **7a**: δ = 194.81 (C_{α}), 140.29 (C_{β})]. However, the ^{13}C- and ^{31}P-NMR spectra of $[PhC{\equiv}CFe(dmpe)_2C{\equiv}CPh]$[25] and $[ClFe(dmpe)_2\text{-}C{\equiv}CPh]$[24a][24c] are rather consistent with the results found for **3a/5a**.

As expected, the bisethynyl complex $[(CO)_5W{=}C(NMe_2)C_{\beta}{\equiv}C_{\alpha}Pd(PEt_3)_2C_{\alpha'}{\equiv}C_{\beta'}H]$ (**10a**) shows two different pairs of resonances for the ethynyl carbons [δ = 166.59 (C_{α}), 122.86 (C_{β}), 103.35 ($C_{\alpha'}$), 96.41 ($C_{\beta'}$)]. The assignment of the C_{α}, $C_{\alpha'}$, C_{β}, and $C_{\beta'}$ resonances is based on the comparison with $[HC{\equiv}CPd(PEt_3)_2C{\equiv}CH]$[21] and **3a**. As a result, the chemical shifts indicate a stronger π-basicity for the $(CO)_5W{=}C(NMe_2)C{\equiv}C$ than for the C≡CH fragment.

The ^{1}H- and ^{13}C-NMR spectra of complexes **8a**, **b** exhibit only one singlet for the cyclopentadienyl rings implying that the protons and the carbons of both rings are equivalent. In contrast, free rotation of the cyclopentadienyl rings is hindered for bulky substituents R [R = $CH_2C(Ph)_2H$ or $CH_2C(Ph)_2CN$] in $[(\eta^5\text{-}C_5H_5)_2Ti(C{\equiv}CR)_2]$[17]. Obviously, the carbene fragment in **8a**, **b** is small enough to avoid a similar effect.

Due to the nuclear spin I = 3/2 of boron the ethynyl resonances in the ^{13}C-NMR spectrum of **11a** appear as quartets. The identification of C_{α} (δ = 147.07) and C_{β} (δ = 101.39) is based on the decreasing size of the J_{BC} coupling constants ($^{1}J_{BC}$ = 71.2 Hz, $^{2}J_{BC}$ = 14.4 Hz). Whereas the ^{1}H-NMR spectrum of complex **11a** shows two distinct resonances for the NMe_2 group that of **12a** shows a doublet at δ = 3.77 ($^{6}J_{PH}$ = 1.2 Hz) and a singlet at δ = 3.61. The doublet is assigned to the methyl group in the *cis*-position with respect to the $W(CO)_5$ fragment at the N−C(carbene) bond. A similar homoallyl coupling between $C{-}CH_3$ and *cis*-$N{-}CH_3$ has already been observed for $[(CO)_5Cr{=}C(Me)NMe_2]$ ($^{5}J_{HH}$ = 0.9 Hz)[32]. Both ethynyl resonances of **12a** appear as doublets. In contrast, $P(C{\equiv}CC_6H_5)_3$ shows a doublet at δ = 109.5 ($^{1}J_{PC}$ = 18 Hz) and a singlet at δ = 82.3[27]. The C_{α} and C_{β} NMR resonances of complex **12a** were unambiguously assigned on the basis of the $^{13}C,^{31}P$ coupling constants. The doublet at higher field (δ = 107.15) with the larger coupling constant $^{1}J_{PC}$ = 11.4 Hz was therefore attributed to C_{α} and that at lower field (δ = 115.17), with the smaller coupling constant $^{2}J_{PC}$ = 8.1 Hz, to C_{β}. Compared to $P(C{\equiv}CPh)_3$ the C_{β} resonance of **12a** is downfield suggesting that the $(CO)_5W{=}C(NMe_2)$ fragment acts as a stronger acceptor than the phenyl group. The resonance in the ^{31}P-NMR spectrum of **12a** (δ = −98.92) resembles that of $P(C{\equiv}CPh)_3$ (δ = −85.1)[27] rather than that of $P(C{\equiv}CH)_3$ (δ = +91)[33] or $P(C{\equiv}CMe)_3$ (δ = +87)[28].

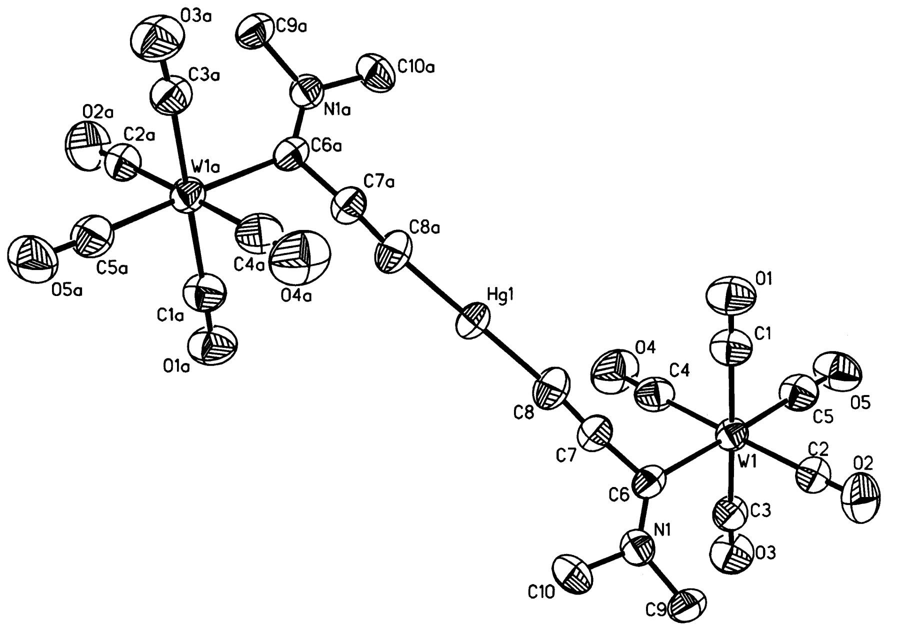
The $^{13}C_{(\alpha,\beta)}$ resonances of **15a**, **b** were assigned on the basis of J_{SnC} coupling constants with $^{1}J_{^{117}SnC,^{119}SnC}$ = 1169.5 Hz, 1118.2 Hz and $^{2}J_{^{117}SnC,^{119}SnC}$ = 218.9 Hz, 209.5 Hz. In contrast to **2−4**, the resonances of the C_{α} and C_{β} carbons of **13a**, **b**, **14a**, and **15a**, **b** are almost independent of the central metal atom [C_{α}, C_{β}: 118.73, 106.14 (**13a**); 117.66, 105.11 (**14a**); 119.47, 109.59 (**15a**)]. Compared to $[M'(C{\equiv}CPh)_4]$[34] or $[M'(C{\equiv}CMe)_4]$[34][35] the C_{α} resonances of complexes **13a**, **b**, **14a**, and **15a**, **b** are downfield.

In summary, the C_{α} resonance in the NMR spectra of the complexes **2−16** is at significantly lower field when compared to the corresponding phenyl-substituted ethynyl complexes[18][21][24c][25][31][36] and the difference $\Delta = \delta(C_{\alpha})-\delta(C_{\beta})$ is much more pronounced. These two trends can be explained by the stronger π-basicity of the $(CO)_5W{=}C(NMe_2)C{\equiv}C$ fragment when compared to that of the phenyl group, which gives rise to an increase in the polarity of the C≡C bond in the direction $M{-}C(\delta{+}){\equiv}C(\delta{-})$.

Structures of 8a, 9a, 12a, and 15a

The structures of the complexes **8a**, **9a**, **12a**, and **15a** were also established by X-ray structural analyses (Figures 1−4). Within error limits the $(CO)_5W{=}C(NMe)_2C{\equiv}C$ unit of the

Figure 1. ORTEP plot of complex **8a** (ellipsoids drawn at 50% level, hydrogens omitted)[a]

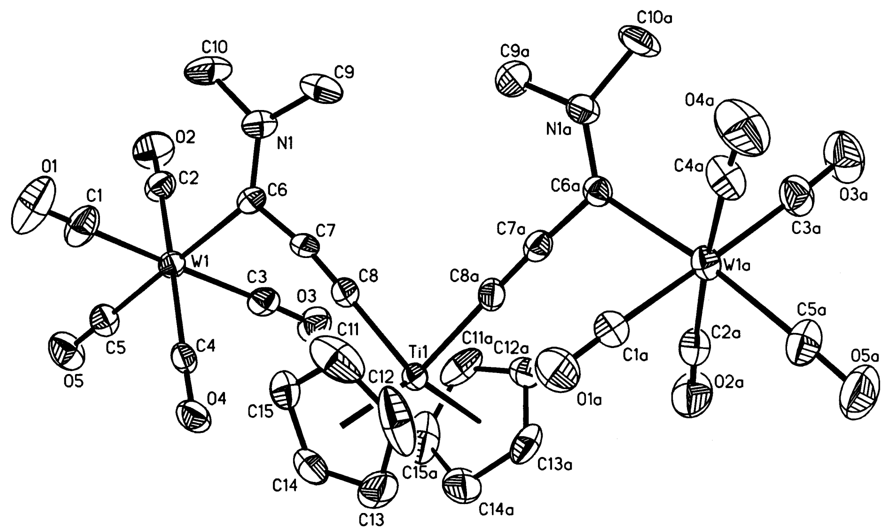


[a] Selected bond lengths [Å] and bond angles [deg]: Hg(1)−C(8) 1.994(9), C(8)−C(7) 1.20(1), C(7)−C(6) 1.43(1), C(8a)−Hg(1)−C(8) 180.0(1), Hg(1)−C(8)−C(7) 175(1), C(8)−C(7)−C(6) 175(1).

complexes **8a**, **9a**, **12a**, and **15a** is identical to that of the heterobimetallic ethynylcarbene complexes [$(CO)_5M{=}C(NMe)_2C{\equiv}CM'L_n$] discussed previously[15]. The carbene carbon atoms (sum of angles: 359.2°−360.0°) as well as the nitrogen atoms (sum of angles: 359.9°−360.0°) of **8a**, **9a**, **12a**, and **15a** are trigonal planar coordinated. The rather long W−C(carbene) distance of the trinuclear complexes **8a** and **9a** [2.237(9) Å (**8a**), 2.244 and 2.250(7) Å (**9a**)], and the rather short C(carbene)−N bond [1.31(1) Å (**8a**), 1.32 and 1.33(1) Å (**9a**)], indicate a considerable double-bond character for the C(carbene)−N bond, similar to [$(CO)_5M{=}C(NMe)_2C{\equiv}CM'L_n$] [W−C(carbene): 2.249(6) to 2.266(5) Å, C(carbene)−N: 1.298(6) to 1.323(8) Å][15]. This double-bond character is also reflected in the two distinct ^{1}H- and ^{13}C-NMR NMe resonances.

In the crystal, complex **8a** shows a centrosymmetric geometry with the Hg(1) atom as the center of symmetry, resulting in a *trans*-coordination of Hg(1) [C(8a)−Hg(1)−C(8): 180.0(1)°] (Figure 1) and a *trans*-configuration of the two bulky $W(CO)_5$ fragments. Also the

Figure 2. ORTEP plot of complex **9a** (ellipsoids drawn at 35% level, hydrogens omitted)[a]



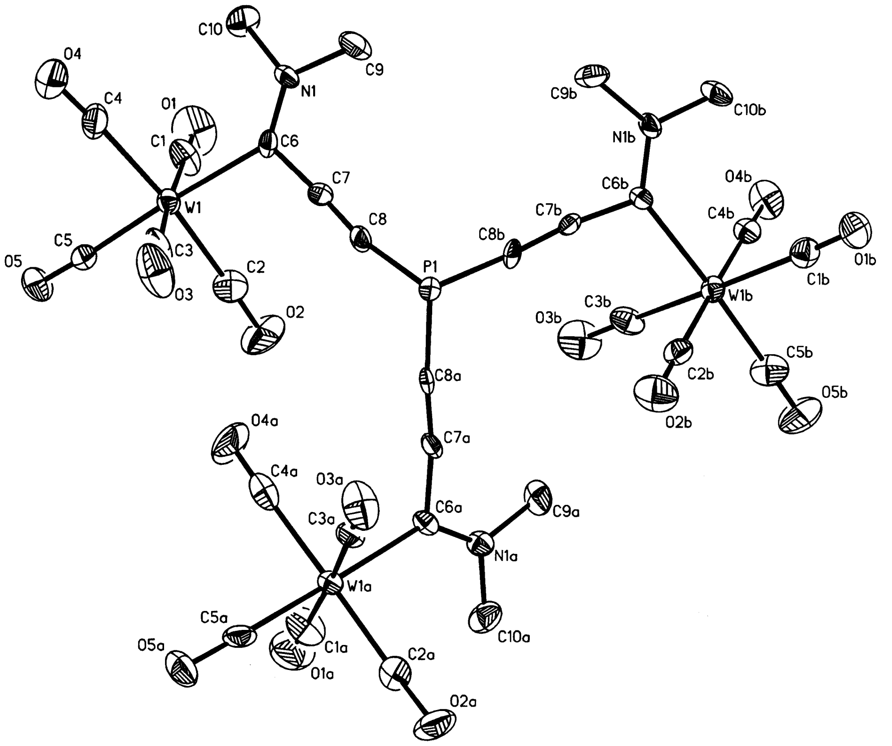
[a] Selected bond lengths [Å] and bond angles [deg]: Ti(1)−C(8a) 2.081(7), Ti(1)−C(8) 2.080(8), C(8a)−C(7a) 1.22(1), C(8)−C(7) 1.22(1), Ti(1)−D(1) 2.029, Ti(1)−D(1a) 2.038, C(7a)−C(6a) 1.41(1), C(7)−C(6) 1.40(1), D(1)−Ti(1)−D(1a) 135.3, Ti(1)−C(8a)−C(7a) 179.1(7), Ti(1)−C(8)−C(7) 178.7(8), C(8a)−C(7a)−C(6a) 176.4(8), C(8)−C(7)−C(6) 172.0(8), C(8a)−Ti(1)−C(8) 97.0(3) [D(1) and D(1a) denote the centroids of the cyclopentadienyl rings].

Hg−C≡C−C(carbene) unit of each σ-ligand is nearly linear [Hg(1)−C(8)−C(7): 175(1)°, C(8)−C(7)−C(6): 175(1)°], similar to the noncentrosymmetric bis(phenylethynyl)mercury-1,10-phenanthroline adduct [$Hg(C{\equiv}CPh)_2{\cdot}C_{12}H_8N_2$] (170, 176° and 173, 176°)[37]. The Hg(1)−C(8) distance and the C≡C distance of **8a** [1.994(9) Å and 1.20(1) Å] resemble those of [$Hg(C{\equiv}CPh)_2{\cdot}C_{12}H_8N_2$) (2.05, 2.03 Å and 1.17, 1.18 Å[37]).

Figure 2 shows that the ethynyl ligands of **9a** are twisted against each other, with the bulky $W(CO)_5$ fragments on the external sides. The two η^5-C_5H_5 ligands are staggered. The CpTiCp angle is typical for many group IV bent metallocene complexes with D(1)−Ti−D(1a) = 135.3°, where D(1)/D(1a) denote the centroids of the cyclopentadienyl rings {for comparison [(η^5-$C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$]: 134.7°[38], [($\eta^5$-$C_5H_4SiMe_3)_2Zr(C{\equiv}CMe)_2$]: 132.6°[39]}. The bite angle C(8)−Ti(1)−C(8a) in **9a** [97.0(3)°] resembles that in [(η^5-$C_5H_4SiMe_3)_2Ti(C{\equiv}CC{\equiv}CFc)_2$] (Fc = ferrocenyl) [97.2(3)°][40] or in [((η^5-$C_5H_4]_2SiMe_2)Ti(C{\equiv}CSiMe_3)_2$] [100.8(5)][41]. The atoms W(1), C(6), N(1), C(7), C(8), Ti(1), C(8a), C(7a), C(6a), N(1a), and W(1a) nearly lie within a plane. The deviations from the plane through C(6), Ti(1) and C(6a) are less than ±0.08 Å. The σ-ethynyl ligands exhibit an almost linear carbon framework [C(8)−C(7)−C(6): 172.0(8)°, C(8a)−C(7a)−C(6a): 176.4(8)°]. The C≡C distances in **9a** [C(8)−C(7): 1.22(1) Å, C(8a)−C(7a): 1.22(1) Å] do not significantly deviate from typical C≡C bond lengths in similar titanocene or zirconocene complexes such as [(η^5-$C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$] [1.203(9), 1.214(6) Å][38], [(η^5-$C_5H_4SiMe_3)_2Zr(C{\equiv}CMe)_2$] [1.206(4) Å][39] or [{(η^5-$C_5H_4)_2SiMe_2$}$Ti(C{\equiv}CSiMe_3)_2$] [1.20(2), 1.21(2) Å][41], or ethynylcarbene complexes such as **1a** (1.196 Å)[42] or [$(CO)_5CrC(OMe)C{\equiv}CPh$] [1.19(3) Å][43]. The Ti(1)−C(8) and Ti(1)−C(8a) distances in **9a** [2.080(8), 2.081(7) Å] are similar to those found in [(η^5-$C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$] [2.124(5), 2.103(5) Å][38] or [(η^5-$C_5H_4SiMe_3)_2Ti$-$(C{\equiv}CC{\equiv}CFc)_2$] (Fc = ferrocenyl) [2.099(7), 2.090(7) Å][40], but are remarkably shorter than those in titanocene complexes with sp^3-hybridized carbon atoms, e.g. such as [(η^5-$C_5H_5)_2Ti(CH_2Ph)_2$] [2.239(6), 2.210(5) Å][44], [(η^5-$C_5H_5)_2TiMe_2$] [2.170(2), 2.181(2) Å][45] and [(η^5-$C_9H_7)_2TiMe_2$] [2.21(2) Å][46]. In the case of [(η^5-$C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$] this is regarded as evidence for some π-conjugation between the acetylide ligands and the d^0-configurated 16-valence electron titanocene fragment[38].

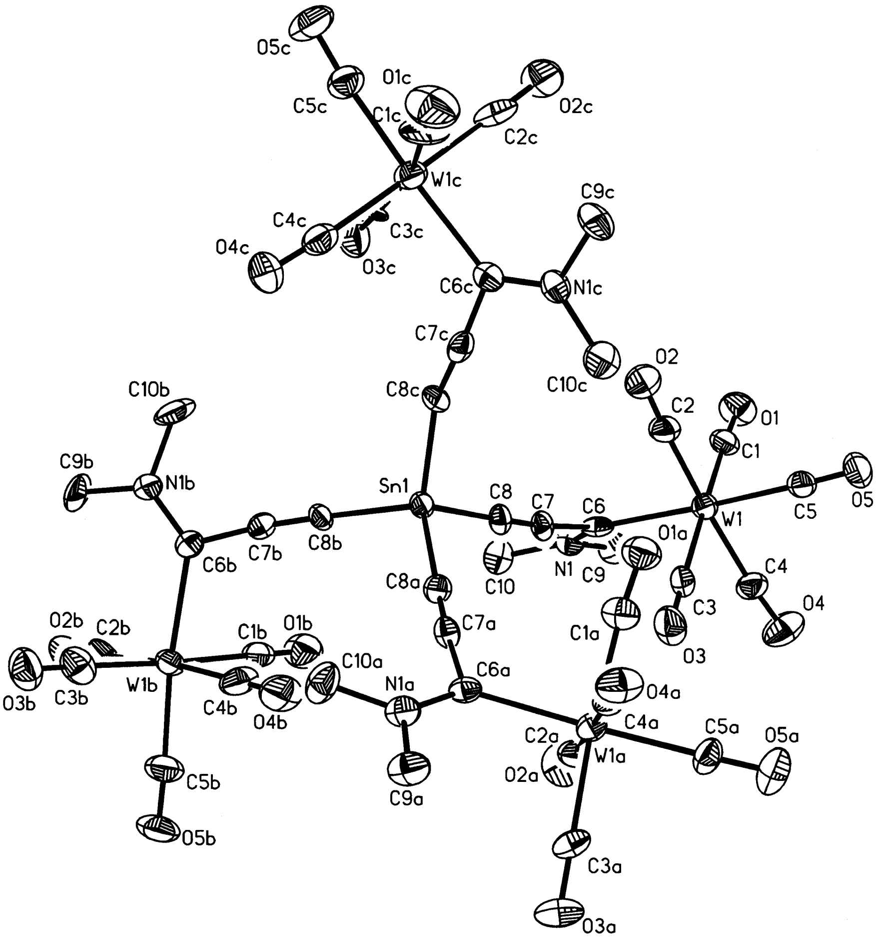
The X-ray structural analyses of **12a** and **15a** also unambiguously establish their structure (Figures 3 and 4). The phosphorus atom in **12a** is pyramidally coordinated, similar to $P(C{\equiv}CPh)_3$[47] or $P(C{\equiv}CH)_3$[48], and the three bond angles at the phosphorus atom [C(8)−P(1)−C(8a): 106.2(7)°, C(8a)−P(1)−C(8b): 102.5(7)°, C(8)−P(1)−C(8b): 103.5(6)°] are similar [$P(C{\equiv}CPh)_3$: 100.7(0.5)°[47], $P(C{\equiv}CH)_3$: 102, 102, 99°[48]]. However, in contrast to the propeller like arrangement of the three phenyl rings in the $P(C{\equiv}CPh)_3$, complex **12a** is not C_3-symmetric in the crystal. In **15a** the bond angles of the central Sn atom are between 107.9(6)° and 111.9(7)° and resemble those of $Sn(C{\equiv}CSiMe_3)_4$ [107.9(1)° to 112.4(3)°][49].

Figure 3. Plot of complex **12a** (ellipsoids drawn at 35% level, hydrogens omitted)[a]



[a] Selected bond angles [deg]: C(8)−P(1)−C(8a) 106.2(7), C(8a)−P(1)−C(8b) 102.5(7), C(8)−P(1)−C(8b) 103.5(6).

Figure 4. Plot of complex **15a** (ellipsoids drawn at 25% level, hydrogens omitted)[a]



[a] Selected bond angles [deg]: C(8)−Sn(1)−C(8a) 108.7(7), C(8a)−Sn(1)−C(8b) 109.2(6), C(8a)−Sn(1)−C(8c) 107.9(6), C(8)−Sn(1)−C(8b) 109.8(7), C(8)−Sn(1)−C(8c) 109.2(6), C(8b)−Sn(1)−C(8c) 111.9(7).

Due to the poor quality of the data set and consequently the large standard deviations of the bond lengths a detailed discussion of the interatomic distances is not feasible.

Conclusions

The coupling of ethynylcarbene complexes $[(CO)_5M{=}C(NMe)_2C{\equiv}CH]$ (M = W, Cr) with metal halides to form heteronuclear complexes with π-conjugated C_3 propynylidene bridges is not restricted to metal monohalides $[XM'(L_n)]$[15] but can also be applied to metal polyhalides $[X_mM'(L_n)]$ ($m = 2-4$). Thus, a wide range of novel π-conjugated tri-, tetra-, and pentanuclear complexes $[\{(CO)_5M{=}C(NMe)_2C{\equiv}C\}_mM'(L_n)]$ are readily accessible by nucleophilic substitution of the lithiated ethynylcarbene complex $[(CO)_5M{=}C(NMe)_2C{\equiv}CLi]$ (M = W, Cr) for the chlorides in $[Cl_mM'(L_n)]$. Transition metals, main group metals as well as other main group elements can be employed as the central linking atom M′.

In *trans*-biscarbene complexes interaction of the two carbene fragments through the ethynyl triple bonds and the d_{xy} and d_{yz} orbitals of the central metal is conceivable. However, the IR and NMR spectra indicate that the mesomeric interaction between the carbene fragments and the central metal is rather small. The central metal $M'(L_n)$ fragment acts as a weak π-donor. With increasing π-donor properties of the $M'(L_n)$ fragment the mesomeric interaction also increases. However, in all cases the influence of the $M'(L_n)$ fragment is inferior to that of the strong π-donor substituent NMe_2 at the carbene carbon.

π-Interaction between the central metal and the acetylide ligands in the pyramidally coordinated complex **12a**, the probably trigonal-planar complex **11a**, and the tetrahedrally coordinated tetrakiscarbene complexes **13**−**15**, is even less pronounced than in the biscarbene complexes.

The π-conjugated polymetallic complexes described here can be considered as monomers for the synthesis of organometallic systems with extended two and three dimensional π-conjugated metal-carbon networks.

Support of this work by the *Fonds der Chemischen Industrie* is gratefully acknowledged. We thank *B. Weibert* for collecting the data sets for the X-ray structural analyses.

Experimental Section

All operations were performed under argon by using standard Schlenk techniques. Solvents were dried by refluxing over CaH_2 (CH_2Cl_2) or sodium/benzophenone ketyl (pentane, Et_2O, THF) and were freshly distilled prior to use. The yields refer to analytically pure substances and were not optimized. Silica gel used for column chromatography (Fa. J. T. Baker, silica gel for flash chromatography) was argon-saturated. For the synthesis of **1a**, **b** by desilylation of $[(CO)_5M{=}C(NMe_2)C{\equiv}CSiMe_3]$[42] (M = W, Cr), KF/THF/MeOH[15] was used instead of Bu_4NF/H_2O[42]. The complexes $[Cl_2Ni(PEt_3)_2]$[50], $[Cl_2Fe(dmpe)_2]$[51], $[Cl_2Ti(\eta^5\text{-}C_5H_5)_2]$[52], and $[ClPd(PEt_3)_2\,C{\equiv}CH]$[53] were prepared according to literature procedures. $[Cl_2Pd(PEt_3)_2]$ and $[Cl_2Pt(PEt_3)_2]$ were purchased from Aldrich. − NMR: Bruker AC 250, Bruker WM 250, Bruker DRX 600, and Jeol JNX 400; chemical shifts are reported relative to internal TMS (^1H and ^{13}C) or external H_3PO_4 (^{31}P). Unless mentioned otherwise, NMR spectra were recorded in $CDCl_3$ at room temperature. Abbreviations: vt = virtual triplet, dvt = double virtual triplet, tvt = triple virtual triplet, vquint = virtual quintet. − IR: Biorad FTS 60. − MS: Finnigan MAT 312. The peaks *m/z* are based on the following isotopes: ^{48}Ti, ^{52}Cr, ^{56}Fe, ^{58}Ni, ^{74}Ge, ^{106}Pd, ^{120}Sn, ^{184}W, ^{195}Pt, ^{202}Hg. − Elemental analyses: Heraeus CHN-O-RAPID.

General Synthetic Route to Compounds **2a**, **b**−**4a**, **b**: 2.00 mmol of *n*BuLi (1.25 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 2.00 mmol of **1a** (0.81 g) or **1b** (0.55 g) in 20 ml of Et_2O. On stirring for 30 min at −80°C, the yellow solution turned cloudy. Then, 1.00 mmol of $[Cl_2M(PEt_3)_2]$ [M = Ni (0.37 g), Pd (0.41 g), Pt (0.50 g)] and 5 ml of THF were added and the dark yellow solution was stirred for 30 min at room temp. The solvent was evaporated in vacuo, the residue dissolved in 5 ml of THF and chromatographed with pentane/THF [4:1 (**2a**,**b**), 7:2 (**3a**,**b**, **4a**,**b**)] at −40°C on silica. Light yellow bands were eluted, which afforded, after removal of the solvent in vacuo and recrystallization from CH_2Cl_2/pentane [3:1 (**2a**,**b**, **3a**,**b**), 4:1 (**4a**,**b**)], the complexes **2a**,**b**−**4a**,**b** as light yellow crystals.

trans-Bis[pentacarbonyl(1-dimethylaminopropynylidene)tungsten]bis(triethylphosphane)nickel (**2a**) *and trans-Bis[pentacarbonyl(1-dimethylaminopropynylidene)chromium]bis(triethylphosphane)nickel* (**2b**): **2a**: Yield: 0.74 g (67%, based on **1a**), m.p. 122°C (dec.). − IR (THF): $\tilde{\nu}(CO)$ = 2058 cm^{-1} w, 1965 w, 1920 vs, 1900 m, $\tilde{\nu}(C{\equiv}C)$ = 2008 cm^{-1} w. − ^1H NMR: δ = 1.15 (tvt, $^{3/5}J_{PH} = {}^3J_{HH}$ = 8.0 Hz, 18 H, CH_2CH_3), 1.77−1.89 (m, 12 H, CH_2), 3.50 (s, 6 H, NCH_3), 3.67 (s, 6 H, NCH_3). − ^{13}C NMR: δ = 8.31 (CH_2CH_3), 16.52 (vt, $^{1/3}J_{PC}$ = 14.6 Hz, CH_2), 44.08 (NCH_3), 51.00 (NCH_3), 131.88 (C_β), 168.40 (t, $^2J_{PC}$ = 38.8 Hz, C_α), 199.45 (s and d, $^1J_{WC}$ = 127.1 Hz, *cis*-CO), 203.88 (*trans*-CO), 223.54 (W=C). − ^{31}P NMR: δ = 22.71. − MS (FAB, NBOH); *m/z* (%): 1102 (7) $[M^+]$, 962 (6), 906 (7) $[M^+ - n\ CO, n = 5, 7]$. − $C_{32}H_{42}N_2NiO_{10}P_2W_2$ (1103.0): calcd. C 34.85, H 3.84, N 2.54; found C 35.09, H 3.78, N 2.42.

2b: Yield: 0.55 g (66%, based on **1b**), m.p. 99°C (dec.). − IR (THF): $\tilde{\nu}(CO)$ = 2049 cm^{-1} w, 1966 w, 1925 vs, 1903 m, $\tilde{\nu}(C{\equiv}C)$ = 2007 cm^{-1} w. − ^1H NMR: δ = 1.14 (tvt, $^{3/5}J_{PH} = {}^3J_{HH}$ = 8.0 Hz, 18 H, CH_2CH_3), 1.76−1.88 (m, 12 H, CH_2), 3.52 (s, 6 H, NCH_3), 3.72 (s, 6 H, NCH_3). − ^{13}C NMR: δ = 8.31 (CH_2CH_3), 16.55 (vt, $^{1/3}J_{PC}$ = 14.5 Hz, CH_2), 45.64 (NCH_3), 48.78 (NCH_3), 130.27 (C_β), 170.75 (t, $^2J_{PC}$ = 39.4 Hz, C_α), 218.43 (*cis*-CO), 224.00 (*trans*-CO), 241.71 (Cr=C). − ^{31}P NMR: δ = 23.19. − $C_{32}H_{42}Cr_2N_2NiO_{10}P_2$ (839.3): calcd. C 45.79, H 5.04, N 3.34; found C 46.00, H 5.09, N 3.25.

trans-Bis[pentacarbonyl(1-dimethylaminopropynylidene)tungsten]bis(triethylphosphane)palladium (**3a**) *and trans-Bis[pentacarbonyl(1-dimethylaminopropynylidene)chromium]bis(triethylphosphane)palladium* (**3b**): **3a**: Yield: 0.81 g (70%, based on **1a**), m.p. 146°C (dec.). − IR (THF): $\tilde{\nu}(CO)$ = 2058 cm^{-1} w, 1966 w, 1920 vs, 1901 m, $\tilde{\nu}(C{\equiv}C)$ = 2032 cm^{-1} w. − ^1H NMR: δ = 1.13 (tvt, $^{3/5}J_{PH} = {}^3J_{HH}$ = 8.1 Hz, 18 H, CH_2CH_3), 1.84−1.96 (m, 12 H, CH_2), 3.53 (s, 6 H, NCH_3), 3.69 (s, 6 H, NCH_3). − ^{13}C NMR: δ = 8.31 (CH_2CH_3), 16.80 (vt, $^{1/3}J_{PC}$ = 14.8 Hz, CH_2), 44.19 (NCH_3), 51.16 (NCH_3), 122.84 (C_β), 163.88 (t, $^2J_{PC}$ = 16.1 Hz, C_α), 199.48 (s and d, $^1J_{WC}$ = 128.5 Hz, *cis*-CO), 204.12 (*trans*-CO), 226.59 (W=C). − ^{31}P NMR: δ = 19.79. − MS (FAB, NBOH); *m/z* (%): 1150 (4) $[M^+]$, 982 (8), 854 (20), 926 (9) $[M^+ - n\ CO, n = 6{-}8]$. − $C_{32}H_{42}N_2O_{10}P_2PdW_2$ (1150.8): calcd. C 33.40, H 3.68, N 2.43; found C 33.76, H 3.60, N 2.17.

3b: Yield: 0.62 g (70%, based on **1b**), m.p. 124°C (dec.). − IR (THF): $\tilde{\nu}(CO)$ = 2050 cm^{-1} w, 1967 w, 1923 vs, 1904 m, $\tilde{\nu}(C{\equiv}C)$ = 2032 cm^{-1} w. − ^1H NMR: δ = 1.12 (tvt, $^{3/5}J_{PH} = {}^3J_{HH}$ = 8.1 Hz, 18 H, CH_2CH_3), 1.83−1.95 (m, 12 H, CH_2), 3.55 (s, 6 H, NCH_3), 3.76 (s, 6 H, NCH_3). − ^{13}C NMR: δ = 8.31 (CH_2CH_3), 16.80 (vt, $^{1/3}J_{PC}$ = 15.0 Hz, CH_2), 45.72 (NCH_3), 48.91 (NCH_3), 121.38 (C_β), 166.38 (t, $^2J_{PC}$ = 16.9 Hz, C_α), 218.38 (*cis*-CO), 224.12 (*trans*-CO), 244.96 (Cr=C). − ^{31}P NMR: δ = 20.19. − $C_{32}H_{42}Cr_2N_2O_{10}P_2Pd\cdot 1/4\ CH_2Cl_2$ (887.1 + 21.2): calcd. C 42.65, H 4.72, N 3.08; found C 42.71, H 4.75, N 3.11.

trans-Bis[pentacarbonyl(1-dimethylaminopropynylidene)tungsten]bis(triethylphosphane)platinum (**4a**) *and trans-Bis[pentacarbonyl(1-dimethylaminopropynylidene)chromium]bis(triethylphosphane)platinum* (**4b**): **4a**: Yield: 0.89 g (72%, based on **1a**), m.p. 169°C (dec.). − IR (THF): $\tilde{\nu}(CO)$ = 2059 cm^{-1} w, 1965 w, 1920 vs, 1902 m, $\tilde{\nu}(C{\equiv}C)$ = 2034 cm^{-1} w. − ^1H NMR: δ = 1.11 (tvt, $^{3/5}J_{PH} = {}^3J_{HH}$ = 8.1 Hz, 18 H, CH_2CH_3), 1.98−2.03 (m, 12 H, CH_2), 3.51 (s, 6 H, NCH_3), 3.69 (s, 6 H, NCH_3). − ^{13}C NMR: δ = 8.09 (s and d, $^3J_{PtC}$ = 24.7 Hz, CH_2CH_3), 16.14 (vt and dvt, $^2J_{PtC}$ = 35.5 Hz, $^{1/3}J_{PC}$ = 17.8 Hz, CH_2), 44.16 (NCH_3), 51.15 (NCH_3), 123.04 (s and d, $^2J_{PtC}$ = 269.7 Hz, C_β), 159.22 (t and dt, J_{PtC} = 977.8 Hz, $^2J_{PC}$ = 14.6 Hz, C_α), 199.43 (s and d, $^1J_{WC}$ = 127.9 Hz, *cis*-CO), 204.17 (s and d, $^1J_{WC}$ = 130.0 Hz, *trans*-CO), 227.32 (W=C). − ^{13}C NMR ([D$_8$]THF): δ = 8.45 (s and d, $^3J_{PtC}$ = 24.7 Hz, CH_2CH_3), 17.04 (vt and dvt, $^2J_{PtC}$ = 36.6 Hz, $^{1/3}J_{PC}$ = 18.3 Hz, CH_2), 44.54 (NCH_3), 51.49 (NCH_3), 124.06 (s and d, $^2J_{PtC}$ = 270.8 Hz, C_β), 159.07 (t and dt, $^1J_{PtC}$ = 980.0 Hz, $^2J_{PC}$ = 14.6 Hz, C_α), 200.39 (s and d, $^1J_{WC}$ = 127.9 Hz, *cis*-CO), 204.25 (*trans*-CO), 226.03 (W=C). − ^{31}P NMR: δ = 10.57 (s and d, $^1J_{PtP}$ = 2318.9 Hz). − MS (FAB, NBOH); *m/z* (%): 1239 (9) $[M^+]$, 1211 (5), 1183 (10), 1071 (9) $[M^+ - n\ CO, n = 1, 2, 6]$. − $C_{32}H_{42}N_2O_{10}P_2PtW_2$ (1239.4): calcd. C 31.01, H 3.42, N 2.26; found C 31.20, H 3.43, N 2.42.

4b: Yield: 0.67 g (69%, based on **1b**), m.p. 142°C (dec.). − IR (THF): $\tilde{\nu}(CO)$ = 2051 cm^{-1} w, 1967 w, 1923 vs, 1902 m, $\tilde{\nu}(C{\equiv}C)$ = 2032 cm^{-1} w. − ^1H NMR: δ = 1.10 (tvt, $^{3/5}J_{PH} = {}^3J_{HH}$ = 8.1 Hz, 18 H, CH_2CH_3), 1.96−2.05 (m, 12 H, CH_2), 3.54 (s, 6 H, NCH_3), 3.73 (s, 6 H, NCH_3). − ^{13}C NMR: δ = 8.10 (s and d, $^3J_{PtC}$ = 25.6 Hz, CH_2CH_3), 16.15 (vt and dvt, $^2J_{PtC}$ = 35.5 Hz, $^{1/3}J_{PC}$ = 17.7 Hz, CH_2), 45.67 (NCH_3), 48.91 (NCH_3), 121.65 (s and d, $^2J_{PtC}$ = 270.8 Hz, C_β), 161.78 (t and dt, $^1J_{PtC}$ = n. f., $^2J_{PC}$ = 14.6 Hz, C_α), 218.33 (*cis*-CO), 224.14 (*trans*-CO), 245.68 (Cr=C). − ^{13}C NMR ([D$_8$]THF): δ = 8.46 (s and d, $^3J_{PtC}$ = 24.7 Hz, CH_2CH_3), 16.99 (vt and dvt, $^2J_{PtC}$ = 35.5 Hz, $^{1/3}J_{PC}$ = 17.8 Hz, CH_2), 46.11 (NCH_3), 49.25 (NCH_3), 122.66 (s and d, $^2J_{PtC}$ = 270.8 Hz, C_β), 161.64 (t and dt, $^1J_{PtC}$ = 978.9 Hz, $^2J_{PC}$ = 14.5 Hz, C_α), 219.43 (*cis*-CO), 224.62 (*trans*-CO), 243.93 (Cr=C). − ^{31}P NMR: δ = 10.85 (s and d, $^1J_{PtP}$ = 2323.9 Hz). − MS (FAB, NBOH); *m/z* (%): 975 (6) $[M^+]$, 919 (16), 891 (8), 835 (31), 807 (15), 779 (89), 751 (11), 723 (37), 695 (100) $[M^+ - n\ CO, n = 2, 3, 5{-}10]$, 577 (55) $[M^+ - PEt_3 - 10\ CO]$. − $C_{32}H_{42}Cr_2N_2O_{10}P_2Pt$ (975.7): calcd. C 39.39, H 4.34, N 2.87; found C 39.44, H 4.42, N 2.74.

Pentacarbonyl{3-[chloro-trans-bis(triethylphosphane)palladio]-1-dimethylaminopropynylidene)}tungsten (**5a**): 2.00 mmol of *n*BuLi (1.25 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 2.00 mmol (0.81 g) of **1a** in 20 ml of Et$_2$O. On stirring the solution for 30 min at −80°C, a white precipitate was formed. Then, 2.00 mmol (0.83 g) of [Cl$_2$Pd(PEt$_3$)$_2$] and 5 ml of THF were added and the dark yellow solution was stirred for 30 min at room temp. After removal of the solvent in vacuo, the residue was dissolved in 5 ml of THF and chromatographed with pentane/THF (7:2) at −40°C on silica. The light yellow band contained **5a**. Yield: 0.95 g (61%, based on **1a**), m.p. 127°C (dec.). − IR (THF): $\tilde{\nu}$(CO) = 2060 cm^{-1} w, 1965 w, 1921 vs, 1901 m, $\tilde{\nu}$(C≡C) = 2045 cm^{-1} w. − ^{1}H NMR: δ = 1.16 (tvt, $^{3/5}J_{PH}$ = $^3J_{HH}$ = 8.1 Hz, 18 H, CH$_2$C*H*$_3$), 1.85−1.97 (m, 12 H, CH$_2$), 3.53 (s, 3 H, NCH$_3$), 3.69 (s, 3 H, NCH$_3$). − ^{13}C NMR: δ = 8.10 (CH$_2$*C*H$_3$), 15.07 (vt, $^{1/3}J_{PC}$ = 14.2 Hz, CH$_2$), 44.28 (NCH$_3$), 51.13 (NCH$_3$), 118.68 (t, $^3J_{PC}$ = 4.7 Hz, C$_\beta$), 149.51 (t, $^2J_{PC}$ = 15.2 Hz, C$_\alpha$), 199.27 (s and d, $^1J_{WC}$ = 127.0 Hz, *cis*-CO), 203.84 (s and d, $^1J_{WC}$ = 129.9 Hz, *trans*-CO), 226.61 (s and d, $^1J_{WC}$ = 86.5 Hz, W=C). − ^{31}P NMR: δ = 19.31. − MS (FAB, NBOH); *m*/*z* (%): 781 (5) [M$^+$], 753 (4), 725 (6), 669 (18), 641 (44) [M$^+$ − *n* CO, *n* = 1, 2, 4, 5]. − $C_{22}H_{36}ClNO_5P_2PdW$ (782.2): calcd. C 33.78, H 4.64, N 1.79; found C 33.73, H 4.53, N 1.72.

trans-Bis[1′,2′-bis(dimethylphosphino)ethane]bis[pentacarbonyl(1-dimethylaminopropynylidene)tungsten]iron (**6a**): 2.00 mmol of *n*BuLi (1.25 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 2.00 mmol (0.81 g) of **1a** in 20 ml of Et$_2$O. On stirring for 30 min at −80°C, the yellow solution turned cloudy. After 1.00 mmol (0.43 g) of [Cl$_2$Fe(dmpe)$_2$] and 5 ml of THF were added, the dark red solution was stirred for 30 min at room temp. The solvent was evaporated in vacuo, the residue was dissolved in 5 ml of CH$_2$Cl$_2$ and chromatographed with pentane/CH$_2$Cl$_2$ (4:1) at −40°C on silica. An orange band was eluted. After removal of the solvent in vacuo, complex **6a** was obtained as an analytically pure orange solid. Yield: 0.41 g (35%, based on **1a**), m.p. 173°C (dec.). − IR (THF): $\tilde{\nu}$(CO) = 2054 cm^{-1} w, 1914 vs, 1895 sh, $\tilde{\nu}$(C≡C) = 1941 cm^{-1} m. − ^{1}H NMR: δ = 1.52 (br. s, 24 H, PCH$_3$), 1.89 (br. s, 8 H, CH$_2$), 3.44 (s, 6 H, NCH$_3$), 3.64 (s, 6 H, NCH$_3$). − ^{13}C NMR: δ = 17.66 (vquint, $^{1/3}J_{PC}$ = 5.9 Hz, PCH$_3$), 30.79 (vquint, $^{1/2/3}J_{PC}$ = 12.9 Hz, CH$_2$), 43.77 (NCH$_3$), 51.53 (NCH$_3$), 135.10 (C$_\beta$), 195.33 (m$_c$, C$_\alpha$), 200.14 (s and d, $^1J_{WC}$ = 126.8 Hz, *cis*-CO), 203.04 (*trans*-CO), 221.59 (W=C). − ^{31}P NMR: δ = 65.66. − MS (FAB, NBOH); *m*/*z* (%): 1164 (25) [M$^+$], 1108 (5), 996 (7), 968 (11), 940 (11), 912 (10), 884 (11), [M$^+$ − *n* CO, *n* = 2, 6−10]. − $C_{32}H_{44}FeN_2O_{10}P_4W_2$ (1164.2): calcd. C 33.02, H 3.81, N 2.41; found C 32.84, H 3.71, N 2.38.

3-{trans-Bis[1′,2′-bis(dimethylphosphino)ethane]chloroferrio}-1-dimethylaminopropynylidene(pentacarbonyl)tungsten (**7a**): 2.00 mmol of *n*BuLi (1.25 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 2.00 mmol (0.81 g) of **1a** in 20 ml of Et$_2$O. On stirring the yellow solution for 30 min at −80°C, a white precipitate was formed. After 2.00 mmol (0.85 g) of [Cl$_2$Fe(dmpe)$_2$] and 10 ml of THF were added, the dark red solution was stirred for 30 min at room temp. and then the solvent was removed in vacuo. The residue was dissolved in 5 ml of CH$_2$Cl$_2$ and chromatographed at −40°C on silica. With pentane/CH$_2$Cl$_2$ (7:2) an orange band was eluted, which afforded the complex **7a** as an analytically pure orange solid, after evaporation of the solvent in vacuo. Yield: 0.46 g (29%, based on **1a**), m.p. 135°C (dec.). − IR (THF): $\tilde{\nu}$(CO) = 2053 cm^{-1} w, 1913 vs, 1891 sh, $\tilde{\nu}$(C≡C) = 1942 cm^{-1} m. − ^{1}H NMR: δ = 1.43 (br. s, 12 H, PCH$_3$), 1.52 (br. s, 12 H, PCH$_3$), 1.94 (br. s, 8 H, CH$_2$), 3.29 (s, 3 H, NCH$_3$), 3.53 (s, 3 H, NCH$_3$). − ^{13}C NMR: δ = 13.91 (vquint, $^{1/3}J_{PC}$ = 5.4 Hz, PCH$_3$), 16.63 (vquint, $^{1/3}J_{PC}$ = 6.5 Hz, PCH$_3$), 30.13 (vquint, $^{1/2/3}J_{PC}$ = 12.6 Hz, CH$_2$), 43.08 (NCH$_3$), 51.11 (NCH$_3$), 140.29 (C$_\beta$), 194.81 (m$_c$, C$_\alpha$), 200.19 (s and d, $^1J_{WC}$ = 127.9 Hz, *cis*-CO), 203.10 (s and d, $^1J_{WC}$ = 128.9 Hz, *trans*-CO), 217.82 (W=C). − ^{31}P NMR: δ = 63.79. − MS (FAB, NBOH); *m*/*z* (%): 795 (36) [M$^+$], 760 (10) [M$^+$ − Cl], 739 (8), 711 (19), 683 (81), 655 (22) [M$^+$ − *n* CO, *n* = 2−5]. − $C_{22}H_{38}ClFeNO_5P_4W$ (795.6): calcd. C 33.21, H 4.81, N 1.76; found C 33.23, H 4.91, N 1.80.

Bis[pentacarbonyl(1-dimethylaminopropynylidene)tungsten]mercury (**8a**): 4.00 mmol of *n*BuLi (2.50 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 2.00 mmol (1.62 g) of **1a** in 40 ml of Et$_2$O. On stirring the yellow solution for 30 min at −80°C, the formation of a white precipitate was observed. 2.00 mmol (0.54 g) of HgCl$_2$ and 10 ml of THF were then added and the dark yellow solution was stirred for 30 min at room temp. The solvent was evaporated in vacuo and the residue was dissolved in 8 ml of CH$_2$Cl$_2$ and chromatographed at −40°C on silica. With pentane/CH$_2$Cl$_2$ (3:1) a yellow band was eluted. Evaporation of the solvent in vacuo and recrystallization from 30 ml of Et$_2$O/pentane (5:2) afforded yellow crystals. Yield: 1.15 g (57%, based on **1a**), m.p. 109°C (dec.). − IR (THF): $\tilde{\nu}$(CO) = 2062 cm^{-1} w, 1972 w, 1926 vs, 1909 sh. − ^{1}H NMR: δ = 3.62 (s, 6 H, CH$_3$), 3.76 (s, 6 H, CH$_3$). − ^{13}C NMR: δ = 46.69 (CH$_3$), 51.72 (CH$_3$), 106.42 (C$_\beta$), 158.67 (C$_\alpha$), 198.56 (s and d, $^1J_{WC}$ = 128.3 Hz, *cis*-CO), 203.93 (s and d, $^1J_{WC}$ = 88.3 Hz, *trans*-CO), 230.77 (s and d, $^1J_{WC}$ = 130.1 Hz, W=C). − MS (FAB, NBOH); *m*/*z* (%): 1010 (57) [M$^+$], 982 (10), 954 (15), 898 (24) [M$^+$ − *n* CO, *n* = 1, 2, 4], 642 (100), 614 (32), 586 (26), 558 (15) [M$^+$ − *n* CO − Hg, *n* = 6−9]. − $C_{20}H_{12}HgN_2O_{10}W_2$ (1008.6): calcd. C 23.82, H 1.20, N 2.78; found C 23.90, H 1.23, N 2.87.

Dicyclopentadienyl{bis[pentacarbonyl(1-dimethylaminopropynylidene)tungsten]}titanium (**9a**) *and Dicyclopentadienyl-{bis[pentacarbonyl(1-dimethylaminopropynylidene)chromium]}-titanium* (**9b**): 4.00 mmol of *n*BuLi (2.50 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 4.00 mmol of **1a** (1.62 g) or **1b** (1.10 g) in 40 ml of Et$_2$O. On stirring the yellow solution for 30 min at −80°C, a white solid precipitated. After 2.00 mmol (0.50 g) of [Cl$_2$Ti(Cp)$_2$] and 10 ml of THF were added, the dark red solution was stirred for 30 min at room temp. The solvent was evaporated in vacuo. The residue was dissolved in 8 ml of CH$_2$Cl$_2$ and chromatographed with pentane/CH$_2$Cl$_2$ [4:1(**9a**), 7:2 (**9b**)] at −40°C on silica. A red band was eluted, which gave red crystals after removal of the solvent in vacuo and recrystallization from 50 ml of Et$_2$O/pentane [4:1(**9a**), 5:2 (**9b**)].

9a: Yield: 1.32 g (67%, based on **1a**), m.p. 142°C (dec.). − IR (THF): $\tilde{\nu}$(CO) = 2058 cm^{-1} w, 1969 w, 1924 vs, 1906 sh. − ^{1}H NMR: δ = 3.40 (s, 6 H, CH$_3$), 3.65 (s, 6 H, CH$_3$), 6.33 (s, 10 H, C$_5$H$_5$). − ^{13}C NMR: δ = 45.64 (CH$_3$), 50.60 (CH$_3$), 112.27 (C$_5$H$_5$), 134.87 (C$_\beta$), 199.03 (s and d, $^1J_{WC}$ = 127.1 Hz, *cis*-CO), 203.95, 204.05 (*trans*-CO, C$_\alpha$), 220.06 (W=C). − MS (FAB, NBOH); *m*/*z* (%): 986 (32) [M$^+$], 958 (4), 930 (20), 902 (10), 874 (15), 846 (25), 818 (100), 790 (18), 762 (41), 734 (25), 706 (21) [M$^+$ − *n* CO, *n* = 1−10]. − $C_{30}H_{22}N_2O_{10}TiW_2$ (986.1): calcd. C 36.54, H 2.25, N 2.84; found C 36.38, H 2.43, N 2.69.

9b: Yield: 0.98 g (68%, based on **1b**), m.p. 131°C (dec.). − IR (THF): $\tilde{\nu}$(CO) = 2049 cm^{-1} w, 1969 w, 1927 vs, 1908 sh. − ^{1}H NMR: δ = 3.43 (s, 6 H, CH$_3$), 3.73 (s, 6 H, CH$_3$), 6.34 (s, 10 H, C$_5$H$_5$). − ^{13}C NMR: δ = 46.99 (CH$_3$), 48.40 (CH$_3$), 112.09 (C$_5$H$_5$), 132.85 (C$_\beta$), 207.19 (C$_\alpha$), 217.84 (*cis*-CO), 223.94 (*trans*-CO), 238.34 (Cr=C). − $C_{30}H_{22}Cr_2N_2O_{10}Ti$ (722.4): calcd. C 49.88, H 3.07, N 3.88; found C 49.96, H 3.03, N 3.87.

Pentacarbonyl{1-dimethylamino-3-[ethynyl-trans-bis(triethylphosphane)palladio]propynylidene}tungsten (**10a**): 3.00 mmol of *n*BuLi (1.88 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 3.00 mmol of **1a** (1.22 g) in 30 ml of Et_2O. On stirring the yellow solution for 30 min at −80°C, the formation of a white solid was observed. 3.00 mmol (1.21 g) of $[ClPd(PEt_3)_2C{\equiv}CH]$ {contaminated with small amounts of $[Cl_2Pd(PEt_3)_2]$} and 10 ml of THF were then added. The dark yellow solution was stirred for 30 min at room temp. and then the solvent was evaporated in vacuo. The residue was dissolved in 6 ml of THF and chromatographed at −40°C on silica. With pentane/THF (4:1) first a light yellow band containing **10a** was eluted. With pentane/THF (7:2) a further light yellow band containing **5a** was eluted. Evaporation of the solvent in vacuo gave complexes **5a** and **10a** as light yellow solids. **5a**: Yield 0.44 g (19%, based on **1a**). − **10a**: Yield: 0.52 g (23%, based on 1**a**), m.p. 87°C (dec.). − IR (THF): $\tilde{\nu}$(CO) = 2059 cm^{-1} w, 1966 w, 1920 vs, 1898 m, $\tilde{\nu}(C{\equiv}C)$ = 2034 cm^{-1} w. − ^1H NMR: δ = 1.08−1.21 (m, 18 H, CH_2CH_3), 1.90−2.02 (m, 12 H, CH_2), 2.19 (t, $^4J_{PH}$ = 1.8 Hz, 1 H, ≡CH), 3.51 (s, 3 H, NCH_3), 3.67 (s, 3 H, NCH_3). − ^{13}C NMR: δ = 8.38 (CH_2CH_3), 16.76 (vt, $^{1/3}J_{PC}$ = 14.5 Hz, CH_2), 44.01 (NCH_3), 51.05 (NCH_3), 96.41 ($C_{\beta'}$), 103.35 (t, $^2J_{PC}$ = 17.4 Hz, $C_{\alpha'}$), 122.86 (C_β), 166.59 (t, $^2J_{PC}$ = 16.6 Hz, C_α), 199.52 (s and d, $^1J_{WC}$ = 126.9 Hz, *cis*-CO), 204.23 (*trans*-CO), 226.32 (W=C). − ^{31}P NMR: δ = 19.29. − MS (70 eV); *m/z* (%): 771 (9) [M^+], 743 (4), 715 (5), 687 (7), 659 (16), 631 (14) [M^+ − *n* CO, *n* = 1−5]. − $C_{24}H_{37}NO_5P_2PdW$ (771.8): calcd. C 37.35, H 4.83, N 1.81; found C 37.47, H 4.87, N 1.93.

Tris[pentacarbonyl(1-dimethylaminopropynylidene)tungsten]boron (**11a**): 3.00 mmol of *n*BuLi (1.88 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 3.00 mmol (1.22 g) of **1a** in 30 ml of Et_2O. On stirring the yellow solution for 30 min at −80°C, the yellow solution turned cloudy. After 1.00 mmol of BBr_3 (1.00 ml of a 1.0 M solution in hexane) was added, the solution was stirred for 30 min at room temp. The solvent of the brown solution was evaporated in vacuo, and the residue was dissolved in 6 ml of CH_2Cl_2 and chromatographed at −40°C on silica. With pentane/CH_2Cl_2 (3:1) a yellow band was eluted, which afforded, after removal of the solvent in vacuo, the complex **11a** as an analytically pure beige solid. Yield: 0.75 g (61%, based on **1a**), m.p. 126°C (dec.). − IR (Et_2O): $\tilde{\nu}$(CO) = 2062 cm^{-1} w, 1980 w, 1925 vs, 1900 sh, $\tilde{\nu}(C{\equiv}C)$ = 2126 cm^{-1} vw. − ^1H NMR ([D_6]acetone): δ = 3.64 (s, 9 H, CH_3), 3.77 (s, 9 H, CH_3). − ^{13}C NMR ([D_6]acetone): δ = 45.42 (CH_3), 51.55 (CH_3), 101.39 (q, $^2J_{BC}$ = 14.4 Hz, C_β), 147.07 (q, $^1J_{BC}$ = 71.2 Hz, C_α), 199.59 (s and d, $^1J_{WC}$ = 128.2 Hz, *cis*-CO), 205.54 (*trans*-CO), 227.86 (W=C). − $C_{30}H_{18}BN_3O_{15}W_3$ (1222.8): calcd. C 29.47, H 1.48, N 3.44; found C 29.30, H 1.57, N 3.31.

Tris[pentacarbonyl(1-dimethylaminopropynylidene)tungsten]phosphorus (**12a**): 3.00 mmol of *n*BuLi (1.88 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 3.00 mmol (1.22 g) of **1a** in 30 ml of Et_2O. On stirring the yellow solution for 30 min at −80°C, a white precipitate was formed. 1.00 mmol (0.14 g) of PCl_3 was then added and the solution stirred for 30 min at room temp. After the solvent of the orange solution was evaporated in vacuo, the residue was dissolved in 6 ml of CH_2Cl_2 and chromatographed with pentane/CH_2Cl_2 (4:1) at −40°C on silica. An orange band containing **12a** was eluted. After removal of the solvent in vacuo and recrystallization from 30 ml of Et_2O/pentane (3:1) the complex **12a** was obtained as orange crystals. Yield: 1.01 g (81%, based on **1a**), m.p. 135°C (dec.). − IR (Et_2O): $\tilde{\nu}$(CO) = 2064 cm^{-1} w, 1977 w, 1934 vs. − ^1H NMR : δ = 3.61 (s, 9 H, CH_3), 3.77 (d, 9 H, $^6J_{PH}$ = 1.19 Hz, CH_3). − ^{13}C NMR: δ = 47.66 (CH_3), 51.60 (CH_3), 107.15 (d, $^1J_{PC}$ = 11.4 Hz, C_α), 115.17 (d, $^2J_{PC}$ = 8.1 Hz, C_β), 197.86 (s and d, $^1J_{WC}$ = 127.2 Hz, *cis*-CO), 203.46 (s and d, $^1J_{WC}$ = 128.9 Hz, *trans*-CO), 226.32 (s and d, $^1J_{WC}$ = 87.0 Hz, W=C). − ^{31}P NMR: δ = −98.92. − MS (FAB, NBOH); *m/z* (%): 1243 (17) [M^+], 1103 (5), 1047 (8), 1019 (11), 991 (11), 963 (10), 935 (9), 907 (17), 879 (18), 851 (10), 823 (13) [M^+ − *n* CO, *n* = 5, 7−15]. − $C_{30}H_{18}N_3O_{15}PW_3$ (1243.0): calcd. C 28.99, H 1.46, N 3.38; found C 29.03, H 1.38, N 3.36.

Tetrakis[pentacarbonyl(1-dimethylaminopropynylidene)tungsten]silicon (**13a**) *and Tetrakis[pentacarbonyl(1-dimethylaminopropynylidene)chromium]silicon* (**13b**): 4.00 mmol of *n*BuLi (2.50 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 4.00 mmol of **1a** (1.62 g) or **1b** (1.10 g) in 40 ml of Et_2O. On stirring the yellow solution for 30 min at −80°C, a white solid precipitated. 1.00 mmol (0.17 g) of $SiCl_4$ was then added, and the solution stirred for 30 min at room temp. The orange solution was filtered over 10 cm of cellite with 200 ml of Et_2O. After evaporation of the solvent in vacuo and recrystallization from 60 ml of Et_2O/pentane (4:1) complexes **13a**, **b** were obtained as orange crystals. **13a**: Yield: 0.99 g (60%, based on **1a**), m.p. 135°C (dec.). − IR (Et_2O): $\tilde{\nu}$(CO) = 2064 cm^{-1} w, 1979 w, 1935 vs, $\tilde{\nu}(C{\equiv}C)$ = 2132 cm^{-1} vw. − ^1H NMR : δ = 3.58 (s, 12 H, CH_3), 3.76 (s, 12 H, CH_3). − ^{13}C NMR: δ = 47.51 (CH_3), 51.77 (CH_3), 106.14 (C_β), 118.73 (C_α), 197.89 (s and d, $^1J_{WC}$ = 128.4 Hz, *cis*-CO), 203.82 (s and d, $^1J_{WC}$ = 128.5 Hz, *trans*-CO), 229.28 (s and d, $^1J_{WC}$ = 88.2 Hz, W=C). − MS (FAB, NBOH); *m/z* (%): 1644 (3) [M^+], 1532 (4), 1392 (4), 1364 (4), 1336 (5), 1308 (5), 1224 (4), 1140 (6), 1112 (6), 1084 (7) [M^+ − *n* CO, *n* = 4, 9−12, 15, 18−20]. − $C_{40}H_{24}N_4O_{20}SiW_4$ (1644.1): calcd. C 29.22, H 1.47, N 3.41; found C 29.30, H 1.69, N 3.27.

13b: Yield: 0.60 g (54%, based on **1b**), m.p. 115°C (dec.). − IR (Et_2O): $\tilde{\nu}$(CO) = 2056 cm^{-1} w, 1981 w, 1938 vs, $\tilde{\nu}(C{\equiv}C)$ = 2130 cm^{-1} vw. − ^1H NMR : δ = 3.64 (s, 12 H, CH_3), 3.89 (s, 12 H, CH_3). − ^{13}C NMR: δ = 48.81 (CH_3), 49.60 (CH_3), 104.12 (C_β), 122.28 (C_α), 216.64 (*cis*-CO), 223.94 (*trans*-CO), 249.88 (Cr=C). − $C_{40}H_{24}Cr_4N_4O_{20}Si$ (1116.7): A correct analysis of **13b** has not yet been obtained.

Tetrakis[pentacarbonyl(1-dimethylaminopropynylidene)tungsten]germanium (**14a**): 4.00 mmol of *n*BuLi (2.50 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 4.00 mmol (1.62 g) of **1a** in 40 ml of Et_2O. On stirring the yellow solution for 30 min at −80°C, the yellow solution turned cloudy. After 1.00 mmol (0.21 g) of $GeCl_4$ was added, the solution was stirred for 30 min at room temp. Then the orange solution was filtered over 10 cm of cellite with 200 ml of Et_2O. Removal of the solvent in vacuo afforded the complex **14a** as an orange solid, which gave orange crystals after recrystallization from 60 ml of Et_2O/pentane (9:2). Yield: 1.00 g (59%, based on **1a**), m.p. 138°C (dec.). − IR (Et_2O): $\tilde{\nu}$(CO) = 2064 cm^{-1} w, 1980 w, 1935 vs, $\tilde{\nu}(C{\equiv}C)$ = 2132 cm^{-1} vw. − ^1H NMR : δ = 3.58 (s, 12 H, CH_3), 3.77 (s, 12 H, CH_3). − ^{13}C NMR: δ = 47.40 (CH_3), 51.80 (CH_3), 105.11 (C_β), 117.66 (C_α), 197.95 (s and d, $^1J_{WC}$ = 127.2 Hz, *cis*-CO), 203.82 (s and d, $^1J_{WC}$ = 128.6 Hz, *trans*-CO), 229.23 (W=C). − MS (FAB, NBOH); *m/z* (%): 1690 (10) [M^+], 1578 (8), 1438 (21), 1298 (16), 1270 (13), 1214 (14), 1158 (24) [M^+ − *n* CO, *n* = 4, 9, 14, 15, 17, 19]. − $C_{40}H_{24}GeN_4O_{20}W_4$ (1688.6): calcd. C 28.45, H 1.43, N 3.32; found C 28.51, H 1.51, N 3.26.

Tetrakis[pentacarbonyl(1-dimethylaminopropynylidene)tungsten]tin (**15a**) *and Tetrakis[pentacarbonyl(1-dimethylaminopropynylidene)chromium]tin* (**15b**): 4.00 mmol of *n*BuLi (2.50 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 4.00 mmol of **1a** (1.62 g) or **1b** (1.10 g) in 40 ml of Et_2O. On stirring

Table 1. Crystallographic data of **8a**, **9a**, **12a**, and **15a**

	8a	**9a**	**12a**	**15a**
Empirical formula	$C_{10}H_6Hg_{0.5}NO_5W \cdot 0.4\ CH_2Cl_2$	$C_{30}H_{22}N_2O_{10}TiW_2$	$C_{30}H_{18}N_3O_{15}PW_3 \cdot 0.25\ CH_2Cl_2$	$C_{40}H_{24}N_4O_{20}SnW_4 \cdot CHCl_3$
Crystal size [mm^3]	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.4	0.3 × 0.3 × 0.3	0.4 × 0.4 × 0.4
Formula mass	538.3	986.1	1264.2	1854.1
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$C2/c$	$P2_1/c$
a [Å]	9.752(2)	12.233(3)	14.791(1)	13.099(2)
b [Å]	8.844(2)	15.806(3)	23.191(2)	30.388(3)
c [Å]	17.033(2)	16.916(3)	25.275(2)	14.398(1)
β [deg]	93.88(1)	98.91(1)	102.31(1)	98.43(1)
V [Å^3]	1466.0(5)	3232(1)	8470(1)	5669(1)
Z	4	4	8	4
Density [g·cm^{-3}]	2.439	2.027	1.983	2.172
Temperature [K]	232	234	244	245
Absorption [mm^{-1}]	13.418	7.551	8.436	8.911
Min/max transm	0.0080/0.0334	0.0613/0.1386	0.0977/0.1630	0.0151/0.0465
Indepdt reflns	3199	7053	8615	12366
Obsd reflns [$F > x\sigma(F)$]	2568 (x = 3)	5394 (x = 4)	6029 (x = 4)	7183 (x = 4)
F(000)	975.20	1864	4692	3424
Index range	+12, +11, ±21	+15, +20, ±21	+18, +29, ±32	+16, +38, ±18
Params refined	180	406	481	638
Final R	0.0386	0.0449	0.0604	0.0627
Final R_w	0.0442	0.0446	0.0644	0.0615
Largest diff peak/hole [e·Å^{-3}]	+1.82/−1.36	+1.07/−1.04	+2.23/−1.65	+2.28/−1.58

the yellow solution for 30 min at −80°C, the formation of a white precipitate was observed. 1.00 mmol (0.26 g) of $SnCl_4$ was then added and the solution stirred for 30 min at room temp. The solvent of the orange solution was evaporated in vacuo, and the residue was dissolved in 8 ml of CH_2Cl_2 and chromatographed at −40°C on silica. With pentane/CH_2Cl_2 [4:1(**15a**), 7:2 (**15b**)] an orange band was eluted, which afforded after removal of the solvent in vacuo complexes **15a**, **b** as analytically pure orange solids. Recrystallization from 30 ml of Et_2O/pentane [3:1(**15a**), 5:2 (**15b**)] gave orange crystals. **15a**: Yield: 1.32 g (76%, based on **1a**), m.p. 136°C (dec.). − IR (Et_2O): $\tilde{\nu}$(CO) = 2064 cm^{-1} w, 1979 w, 1933 vs, $\tilde{\nu}$(C≡C) = 2118 cm^{-1} vw. − ^{1}H NMR : δ = 3.59 (s, 12 H, CH_3), 3.76 (s, 12 H, CH_3). − ^{13}C NMR: δ = 47.32 (CH_3), 51.74 (CH_3), 109.59 (s and 2 d, $^2J_{^{117}SnC,^{119}SnC}$ = 218.9 Hz, 209.5 Hz, C_β), 119.47 (s and 2 d, $^1J_{^{117}SnC,^{119}SnC}$ = 1169.5 Hz, 1118.2 Hz, C_α), 198.07 (s and d, $^1J_{WC}$ = 128.4 Hz, *cis*-CO), 203.89 (s and d, $^1J_{WC}$ = 128.7 Hz, *trans*-CO), 229.41 (s and d, $^1J_{WC}$ = 88.2 Hz, W=C). − MS (FAB, NBOH); m/z (%): 1736 (10) [M$^+$], 1512 (3), 1484 (6), 1456 (7), 1428 (8), 1400 (12), 1372 (14), 1344 (17), 1316 (13), 1288 (17), 1260 (12), 1232 (13), 1204 (13), 1176 (13) [M$^+$ − n CO, n = 8−20]. − $C_{40}H_{24}N_4O_{20}SnW_4$ (1734.7): calcd. C 27.70, H 1.39, N 3.23; found C 27.80, H 1.43, N 3.15.

15b: Yield: 0.86 g (71%, based on **1b**), m.p. 112°C (dec.). − IR (Et_2O): $\tilde{\nu}$(CO) = 2057 cm^{-1} w, 1982 w, 1937 vs, $\tilde{\nu}$(C≡C) = 2115 cm^{-1} vw. − ^{1}H NMR : δ = 3.65 (s, 12 H, CH_3), 3.88 (s, 12 H, CH_3). − ^{13}C NMR: δ = 48.65 (CH_3), 49.56 (CH_3), 107.68 (s and 2 d, $^2J_{^{117}SnC,^{119}SnC}$ = 219.9 Hz, 210.3 Hz, C_β), 123.05 (s and 2 d, $^1J_{^{117}SnC,^{119}SnC}$ = 1167.5 Hz, 1115.7 Hz, C_α), 216.84 (*cis*-CO), 223.97 (*trans*-CO), 250.09 (Cr=C). − $C_{40}H_{24}Cr_4N_4O_{20}Sn$ (1207.3): calcd. C 39.79, H 2.00, N 4.64; found C 39.67, H 2.19, N 4.64.

X-ray Structural Analyses of **8a**, **9a**, **12a**, *and* **15a**: Single crystals were grown from pentane/Et_2O [2:5 (**8a**), 1:4 (**9a**), 1:3 (**12a**, **15a**)], respectively, and mounted in a glass capillary. All crystal data were collected on a Siemens P4 diffractometer (Wyckoff scan, scan range 4° < 2θ < 54°, scan speed variable: 4 to 30° min^{-1} in ω) with a graphite monochromator (Mo-$K\alpha$, λ = 0.71073 Å). Semi-empirical absorption corrections were employed (ψ-scans with 10 reflections). The structures were solved with Patterson methods using the Siemens SHELXTL PLUS program package. The positions of the hydrogen atoms were calculated by assuming ideal geometry (d_{C-H} = 0.96 Å), and their coordinates were refined together with the attached carbon atoms as a "riding model". The positions of all other atoms were refined anisotropically by full-matrix least-squares techniques. Complete lists of atom coordinates and thermal parameters were deposited[54].

☆ Dedicated to Professor *Warren Roper* on the occasion of his 60th birthday.

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