Heterobimetallic Complexes with a Propynylidene C_3-Bridge: General Synthetic Routes to Bimetallic Ethynylcarbene Complexes

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Received November 15, 1996

Keywords: Heterobimetallic complexes / Carbene complexes / Alkynes / Coupling reaction / Bridging ligands

Sequential reaction of the dimethylamino(trimethylsilylethynyl)carbene complexes $[(CO)_5M'{=}C(NMe_2)C{\equiv}CSiMe_3]$ [M' = W (**1a**), M' = Cr (**1b**)] with KF/THF/MeOH, *n*BuLi and transition metal halides, $[XML_n]$, affords heterobimetallic propynylidene complexes of the type $[(CO)_5M'{=}C(NMe_2)C{\equiv}CML_n]$ [ML_n = $Ni(PPh_3)Cp$ (**4a**, **b**), $Ni(PMe_2Ph)_2(Mes)$ (Mes = 2,4,6-$C_6H_2Me_3$) (**5a**), $Rh(CO)(PPh_3)_2$ (**6a**), $Fe(CO)_2Cp$ (**7a**, **b**)]. In contrast, reaction of **1a** with MeLi · LiBr and $[IFe(CO)_2Cp]$ yields the novel *N*-metallated complex $[(CO)_5W{=}C\{N(Me)Fe(CO)_2Cp\}C{\equiv}CSiMe_3]$ (**8a**). The complexes $[(CO)_5M'{=}C(NMe_2)C{\equiv}CML_n]$ [ML_n = $Fe(CO)_2Cp$ (**7a**, **b**), $Ru(CO)_2Cp$ (**10a**, **b**), $Ru(CO)(PPh_3)Cp$ (**11a**), $Mn(CO)_5$ (**12a**), $Re(CO)_5$ (**13a**)] are accessible by Pd-catalyzed coupling of the *C*-stannylated carbene complexes $[(CO)_5M'{=}C(NMe_2)C{\equiv}CSnBu_3]$ (**9a**, **b**) with $[XML_n]$. The related monomethylaminocarbene complexes $[(CO)_5M'{=}C(NHMe)C{\equiv}CSnBu_3]$ (**16a**, **b**), obtained by stannylation of $[(CO)_5M'{=}C(NHMe)C{\equiv}CH]$ (**15a**, **b**) with Bu_3SnNEt_2, react with $[IFe(CO)_2Cp]$ to give the bimetallic complexes $[(CO)_5M'{=}C(NHMe)C{\equiv}CFe(CO)_2Cp]$ (**17a**, **b**). The complexes **4a**, **5a**, **7a** and **10a** were characterized by X-ray structural analyses. The spectroscopic and structural data suggest that the two metal centers in **4**–**7**, **10**–**13** and **17** interact only weakly.

Introduction

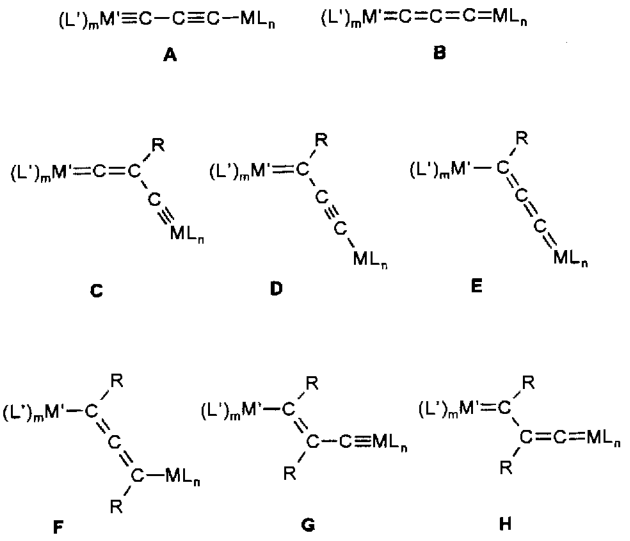
Bi- and polynuclear transition-metal complexes containing unsaturated conjugated carbon bridges have recently attracted considerable interest, since electronic communication between the metal centers should lead to unusual physical and chemical properties[1]. Carbon-bridged bimetallic π-conjugated complexes of the type $[(L')_mM'C_xML_n]$ were for example proposed as a new class of one-dimensional molecular wires[1d]. Binuclear complexes with different metal ligand end groups at a conjugated π-system should exhibit second-order nonlinear optical (NLO) properties.

To date, binuclear complexes with an even number of carbon atoms linking the metal centers have been more readily accessible than those with an odd number of carbon atoms[1a]. For C_3-bridged binuclear complexes, $[(L')_mM'[C_3R_y]ML_n]$ ($y = 0-2$), several types are conceivable (Scheme 1: see **A**–**H**).

The first complex of type **A**/**B** was reported by Gladysz et al. in 1993[2] [$(L')_mM'$ = $Cp^*(NO)(PPh_3)Re$, ML_n = $Mn(CO)_2Cp^+$]. Only recently, Templeton et al.[3] also prepared some C_3-bridged molybdenum and tungsten complexes.

Only one example of a type-**C** complex is known, namely the anionic $\{[W]C(CH)C[Mo]\}^-$ {[W] = $W(CO)_2Tp'$, [Mo] = $Mo(CO)_2Tp'$, Tp' = tris(pyrazolyl)borate}, generated by deprotonation of $[W]{\equiv}C(CH_2)C{\equiv}[Mo]$[3] with KO*t*Bu. Examples of types **D**/**E** are also very scarce. Gladysz et al.[2,4] synthesized a few complexes by reaction of $[Cp^*(NO)(PPh_3)ReC{\equiv}C^-Li^+]$ with $[L_nM{-}CO]$ = $[Mn(CO)_3Cp]$, $[Fe(CO)_5]$, $[W(CO)_6]$ or $[Re_2(CO)_{10}]$ and subsequent alkylation of the resulting metallates with $[Me_3O]BF_4$. Binuclear complexes with a conjugated C_3R_2-bridging ligand (types **F**–**H**) are as yet unknown.

Scheme 1

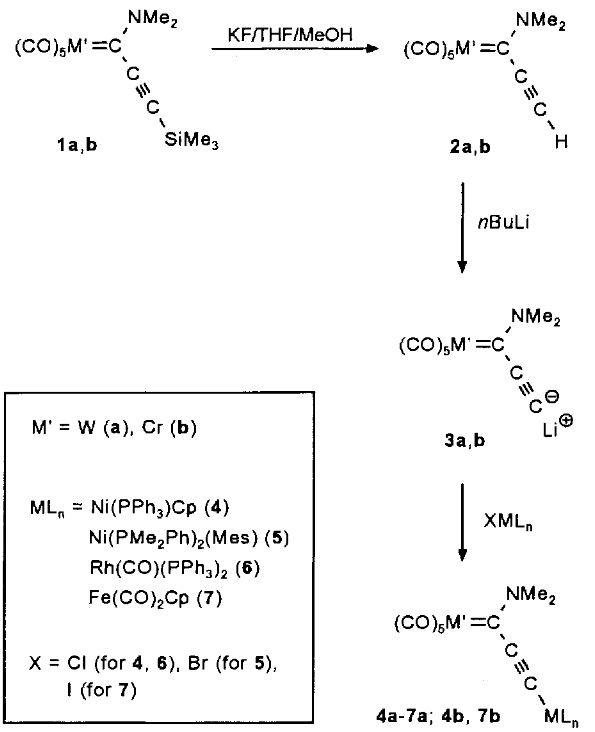


There are two straightforward approaches for the synthesis of binuclear complexes with a C_3-bridge, starting from smaller units: (a) coupling of an $(L')_mM'C_2$ fragment with a CML_n fragment, or (b) coupling of an $(L')_mM'C_3$ fragment with an ML_n fragment. All previously prepared binuclear complexes with a C_3- or C_3R-bridge have been synthesized via route (a). We now report on new routes to heterobinuclear C_3R-bridged complexes. These syntheses follow route (b) by using alkynylcarbene complexes and organometallic halides as the starting compounds and offer a fairly general access to propynylidene complexes, which might serve as precursors for binuclear complexes with a "naked" C_3-linkage.

Results and Discussion

Alkoxy(ethynyl)carbene complexes, $[(CO)_5M'=C(OR)-C\equiv CH]$ (M' = Cr, W), seemed to be the starting materials of choice for the synthesis of C_3R-bridged binuclear complexes. However, these alkoxy-substituted carbene complexes proved to be too unstable and readily decomposed in solution even at low temperatures. The decomposition was faster than the envisaged coupling reaction with metal halides. In contrast, amino(ethynyl)carbene complexes are more stable due to the stabilizing effect of the amino substituent at the carbene carbon atom, and can be isolated[5]. The acetylenic proton in the pentacarbonyl[dimethylamino-(ethynyl)carbene]metal complexes **2a**, **b** was shown to be acidic[5], similar to that in terminal organic alkynes. Complexes **2a**, **b**[5] were obtained by desilylation of $[(CO)_5M'=C(NMe_2)C\equiv CSiMe_3]$ (**1a**, **b**) with KF/THF/MeOH. Deprotonation of **2a**, **b** with *n*BuLi at −80 °C in THF or Et_2O gave the lithiated complexes **3a**, **b**. These were treated in situ with the corresponding transition metal halide (Scheme 2).

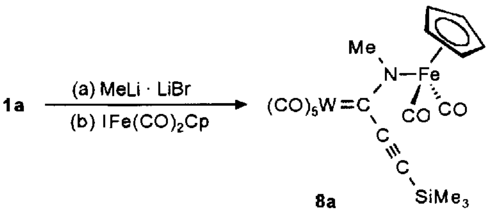
Scheme 2



Nucleophilic substitution of the halide in $[XML_n]$ by the anion in **3a**, **b** afforded the neutral heterobinuclear complexes **4**−**7** in 78−85% yield after chromatography. Metal halides of group 10 $\{[ClNi(PPh_3)Cp]$ and $[BrNi(PMe_2Ph)_2(Mes)]$ (Mes = 2,4,6-$C_6H_2Me_3$)$\}$, of group 9 $\{[ClRh(CO)(PPh_3)_2]\}$, and of group 8 $\{[IFe(CO)_2Cp]\}$ were successfully used. However, only decomposition of **3a**, **b** was observed when $[ClRu(CO)_2Cp]$, $[ClRu(PPh_3)_2Cp]$, $[BrMn(CO)_5]$ or $[BrRe(CO)_5]$ were employed as substrates. Obviously, decomposition of **3a**, **b** was faster than substitution of $(CO)_5M'=C(NMe_2)C\equiv C$ for the halide in $[XML_n]$.

An attempt to shortcut the sequence **1a** → **2a** → **3a** → **7a** through direct lithiation of **1a** led to an unexpected result. When **1a** was treated with MeLi · LiBr and then with $[IFe(CO)_2Cp]$ instead of **7a**, the *N*-[dicarbonyl(cyclopentadienyl)iron]-substituted complex **8a** was obtained in 24% yield (Scheme 3). The structure of **8a** was unambiguously established by (a) the appearance of two singlets for the X−Me groups at δ = 0.33 (X = Si) and 3.70 (X = N) with a relative intensity of 3:1 in the ^1H-NMR spectrum, and (b) the ^{13}C resonances of the alkynyl fragment at δ = 114.99 ($C\equiv CSi$) and 125.92 ($\equiv CSi$) [for comparison: $\delta(C\equiv CX)$ = 106.06 (**1a**, X = Si)[5] and 127.79 (**7a**, X = Fe); $\delta(\equiv CX)$ = 134.16 (**1a**, X = Si)[5] and 148.77 (**7a**, X = Fe)]. Complex **8a** is presumably formed by MeLi-induced abstraction of "Me^+" from the NMe_2 group in **1a** followed by replacement of the iodide ligand in $[IFe(CO)_2Cp]$ by the resulting anion. Binuclear complexes with a =C(R)O− group linking the metal centers (oxycarbenemetal complexes) have been known for a long time[6,7]; *N*-transition-metal-substituted aminocarbene complexes [=C(R)−N(R)− as the bridging ligand] are new.

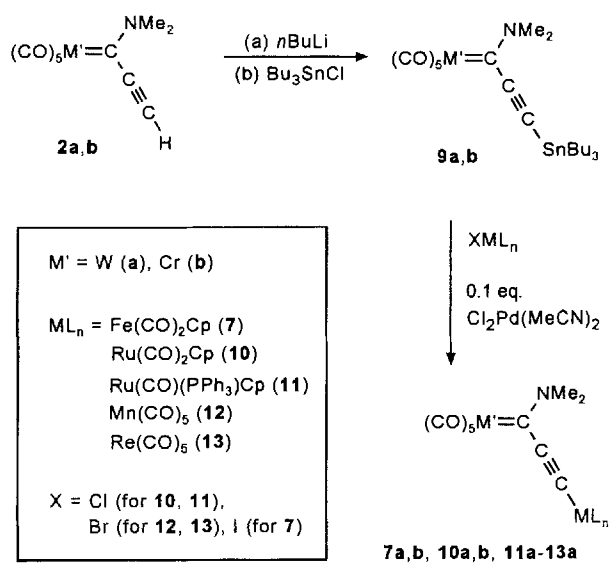
Scheme 3



The problems encountered in the reactions of **3a**, **b** with halides of manganese, rhenium and ruthenium (Scheme 2) could be circumvented by using the [(tributylstannyl)ethynyl]carbene complexes **9a**, **b**. Reaction of **3a**, **b** with Bu_3SnCl gave **9a**, **b** in 79% (**9a**) and 81% yield (**9b**), respectively, as isolable oils which were stable at room temperature under nitrogen. Coupling of **9a**, **b** with metal halides $[XML_n]$ using Stille conditions (0.1 equiv. of $[Cl_2Pd(MeCN)_2]$ as the catalyst)[8] afforded, within one to three days at room temperature, the complexes **7a**, **b**, **10a**, **b** and **11a**−**13a** in good to moderate yields (Scheme 4).

The $Fe(CO)_2Cp$-substituted complexes **7a**, **b** were prepared by both methods. The direct route (Scheme 2) gave slightly higher yields than the route via **9a**, **b** (Scheme 4). When the iron in the metal halide was replaced by its higher homologue ruthenium, the yields dropped. When both CO ligands in $[ClRu(CO)_2Cp]$ were replaced by PPh_3 ligands, three days instead of one were required for completion of the reaction with **9a**. Complex **11a** was isolated in 22%

Scheme 4

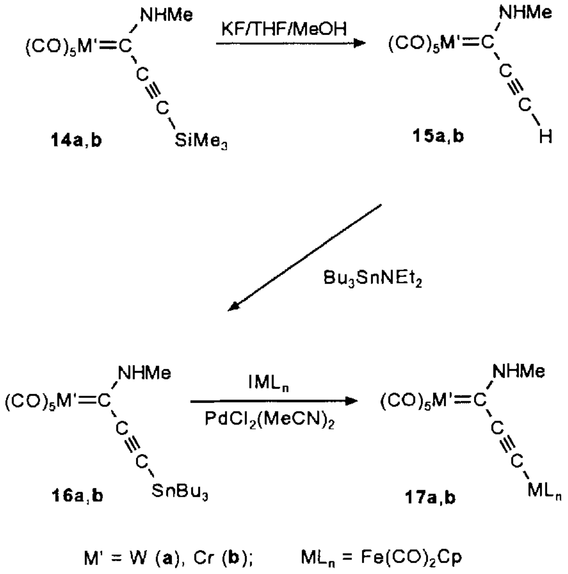


yield. The expected bis(phosphane)-substituted complex $[(CO)_5W{=}C(NMe_2)C{\equiv}CRu(PPh_3)_2Cp]$ was not detected. Clearly, coupling of **9a** with $[ClRu(PPh_3)_2Cp]$ had proceeded with concomitant substitution of one of the two coordinated PPh_3 ligands by CO, either in the metal halide or in the possibly generated $[(CO)_5W{=}C(NMe_2)C{\equiv}CRu(PPh_3)_2Cp]$. Carbon monoxide was most likely derived from decomposition of **9a** due to the long reaction time. The loss of a bulky PPh_3 ligand from $[Cp(PPh_3)_2RuX]$ complexes is well-established[9]. A phosphane/CO exchange was also observed in the reaction of $[Cp(PPh_3)_2RuCl]$ with $[Fe_2(CO)_9]$ at room temperature[10].

In contrast to **3a**, **b**, complex **9a** also reacted with $[BrMn(CO)_5]$ and $[BrRe(CO)_5]$ to form the corresponding binuclear compounds **12a** and **13a**, albeit in modest to rather low yields.

Binuclear monoaminopropynylidene complexes were prepared by following the route summarized in Scheme 5. The starting complexes **14a**, **b** were obtained by aminolysis of $[(CO)_5M'{=}C(OMe)C{\equiv}CSiMe_3]$ with H_2NMe. Desilylation of **14a**, **b** with KF/THF/MeOH afforded the aminocarbene complexes **15a**, **b**. It was not possible to selectively deprotonate the alkynyl group of **15a**, **b**. When *n*BuLi was added to solutions of **15a**, **b**, predominantly decomposition of the complexes was observed. However, on treatment of **15a**, **b** with Bu_3SnNEt_2 the new [(tributylstannyl)ethynyl]carbene complexes **16a**, **b** were formed as yellow oils (Scheme 5). In the reaction of **15a**, **b** with Bu_3SnNEt_2, $HNEt_2$ was liberated. The yield of **16a**, **b** was low [21% (**16a**), 14% (**16b**)] since Michael addition of $HNEt_2$ to the C≡C bond could not completely be avoided. Michael addition of amines to the C≡C bond has also been observed with other alkynylcarbene complexes[5,11]. Transmetallation of **16a**, **b** with $[IFe(CO)_2Cp]$, again using Stille conditions, finally led to the complexes **17a**, **b** in 81% and 68% yield, respectively (Scheme 5). For **14a**, **b**–**17a**, **b**, the *anti* isomer [*anti* arrangement of $(CO)_5M'$ and Me with respect to the C(carbene)–N bond] was found to be the exclusive product, as indicated by NMR spectroscopy (for the structural assignment of *syn* and *anti* isomers of $[(CO)_5M{=}C(NHMe)C{\equiv}CPh]$ complexes (M = Cr, W) by NMR spectroscopy see ref.[11b]).

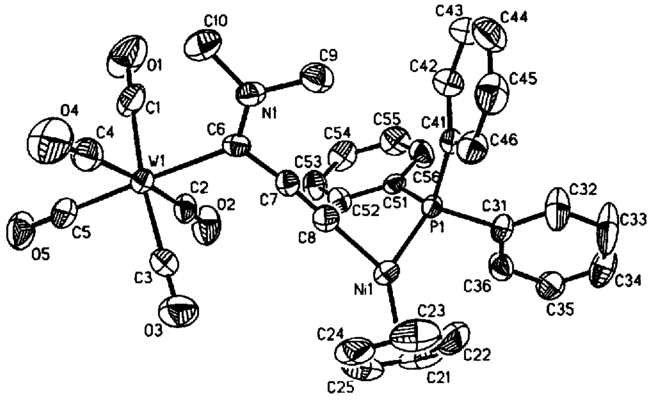
Scheme 5



All new complexes **4**–**17** were characterized by spectroscopic means and by elemental analyses. At room temperature, compound **5a** decomposes in solution within several hours, although it is stable in the solid state. All other complexes were found to be stable at room temperature, both in solution and in the solid state. The positions of the ν(CO) absorptions of the pentacarbonyl metal moiety in **4**–**7**, **10**–**13** and **17** are only marginally influenced by variation of the ML_n fragment. However, due to the strong π-basic properties of the transition metal ligand fragment, the A^1 (*trans*) and the E absorptions are at significantly smaller wavenumbers than those of the trimethylsilyl-, tributylstannyl- and unsubstituted ethynylcarbene complexes. With increasing back-bonding capacity of the ML_n substituent, the ν(C≡C) absorption shifts towards smaller wavenumbers. The considerable drop of the ν(C≡C) band of the binuclear complexes when compared to the corresponding phenylethynyl complexes $[Ph{-}C{\equiv}C{-}ML_n]$ [ML_n = $Ni(PPh_3)Cp$[12], $Ni(PMe_2Ph)_2(Mes)$[13], $Rh(CO)(PPh_3)_2$[14], $Fe(CO)_2Cp$[15], $Ru(CO)(PPh_3)Cp$[16], $Mn(CO)_5$[17], $Re(CO)_5$[17]] or to $[MeOOC{-}C{\equiv}C{-}Fe(CO)_2Cp]$[18] suggests that the $(CO)_5M'{=}C(NMe_2)$ fragment acts as a strong acceptor.

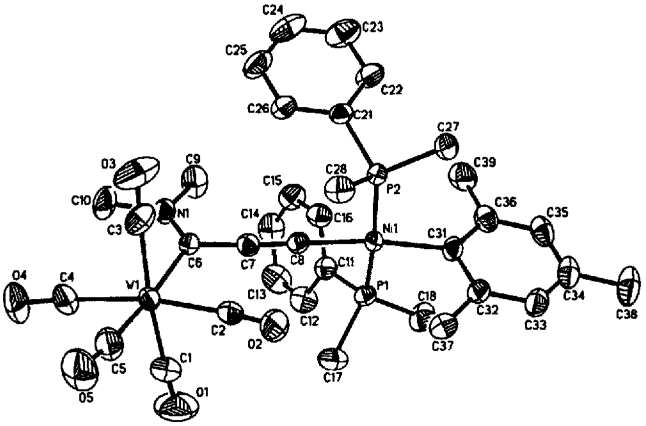
The resonance of the carbene carbon atom in the ^{13}C-NMR spectra of the binuclear complexes is at rather high field (in the region δ = 243–253 for M' = Cr and δ = 221–232 for M' = W), but compares well with that usually observed for aminocarbene complexes. As expected from the trends in the IR spectroscopic data, substitution of a transition metal ligand fragment for H, $SiMe_3$ or $SnBu_3$ causes an upfield shift of the $C_{Carbene}$ resonance. A positive correlation between the resonance of the carbene carbon

Figure 1. ORTEP plot of complex **4a** (ellipsoids drawn at 50% level, hydrogen atoms omitted)[a]



[a] Selected bond lengths [Å] and angles [°]: W(1)−C(6) 2.266(5), C(6)−N(1) 1.298(6), C(6)−C(7) 1.424(8), C(7)−C(8) 1.203(8), W(1)−C(5) 2.001(6), W(1)−C(6)−C(7) 114.3(3), W(1)−C(6)−N(1) 130.1(4), C(6)−C(7)−C(8) 173.8(6).

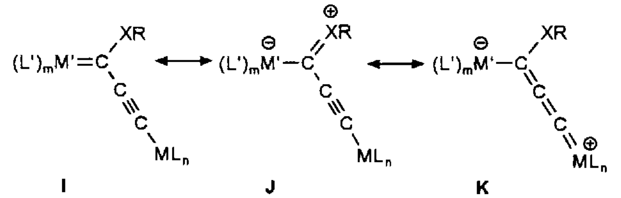
Figure 2. ORTEP plot of complex **5a** (ellipsoids drawn at 50% level, hydrogen atoms omitted)[a]



[a] Selected bond lengths [Å] and angles [°]: W(1)−C(6) 2.255(4), C(6)−N(1) 1.312(6), C(6)−C(7) 1.414(5), C(7)−C(8) 1.217(5), W(1)−C(5) 1.975(5), W(1)−C(6)−C(7) 115.3(3), W(1)−C(6)−N(1) 129.3(2), C(6)−C(7)−C(8) 173.4(4).

atom and the ν(C≡C) absorption in $(CO)_5W{=}C(NMe_2)C_\beta{\equiv}C_\alpha ML_n$ is observed, while an inverse correlation exists between the $C_{Carbene}$ resonance and the resonances of C_α and C_β. In the series **5a**, **6a**, **11a**, **7a**, **12a** and **13a** the resonances of the atoms C_α and C_β shift towards *lower* field and the $C_{Carbene}$ signal shifts towards *higher* field. This indicates increasing importance of the metallacumulene resonance from **K** (Scheme 6).

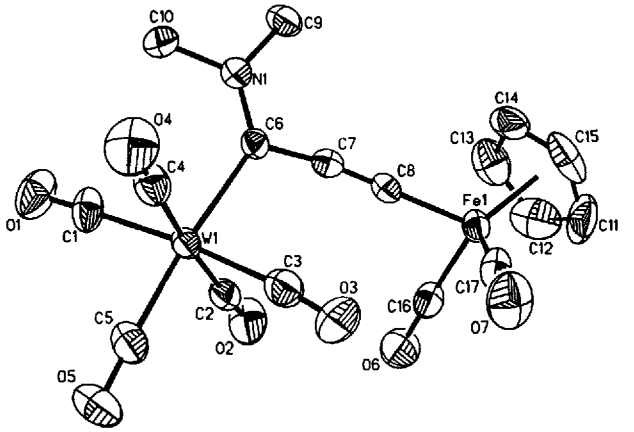
Scheme 6



I J K

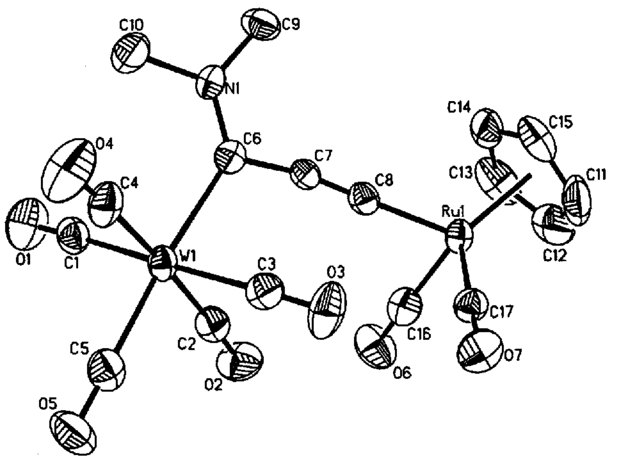
XR = NMe₂, OMe

Figure 3. ORTEP plot of complex **7a** (ellipsoids drawn at 50% level, hydrogen atoms omitted)[a]



[a] Selected bond lengths [Å] and angles [°]: W(1)−C(6) 2.251(6), C(6)−N(1) 1.321(8), C(6)−C(7) 1.414(7), C(7)−C(8) 1.212(7), W(1)−C(5) 1.975(7), W(1)−C(6)−C(7) 113.9(4), W(1)−C(6)−N(1) 130.5(4), C(6)−C(7)−C(8) 171.8(6).

Figure 4. ORTEP plot of complex **10a** (ellipsoids drawn at 50% level, hydrogen atoms omitted)[a]



[a] Selected bond lengths [Å] and angles [°]: W(1)−C(6) 2.249(6), C(6)−N(1) 1.323(8), C(6)−C(7) 1.424(8), C(7)−C(8) 1.204(8), W(1)−C(5) 1.981(7), W(1)−C(6)−C(7) 113.6(4), W(1)−C(6)−N(1) 131.1(4), C(6)−C(7)−C(8) 170.5(6).

Structures of 4a, 5a, 7a and 10a

The structures of the complexes **4a**, **5a**, **7a** and **10a** were additionally established by X-ray structural analyses (Figures 1−4). Within error limits, the central $W{=}C(NMe_2)C{\equiv}C-$ unit is identical in all the binuclear complexes. The C(6)−C(7)−C(8)−M fragment is almost linear, the C(6)−C(7)−C(8) angle varies between 170.5(6) (**10a**) and 173.8(6)° (**4a**), and the C(7)−C(8)−M angle varies between 175.0(5) (**4a**) and 179.4(5)° (**7a**). The *W*-bonded carbon atom C(6) and the nitrogen atom N(1) are planar coordinated [sum of angles: 359.9−360.0° at C(6), 360.0° at N(1)]. The W(1)−C(6) distance, which is in the range of 2.249(6) (**10a**) to 2.266(5) Å (**4a**), is longer than that in the aminocarbene complex $[(CO)_5W{=}C(NHMe)Ph]$ [2.186(22) Å][19] or in **1a** (2.224 Å)[5]. The C(6)−N(1) bond is rather short [1.298(6) (**4a**) to 1.323(8) Å (**10a**)] as compared to a

C(sp^2)–N(sp^2) single bond length (1.416 Å)[20] but is similar to that in [$(CO)_5W{=}C(NHMe)Ph$] (1.299(26) Å)[19]. This indicates considerable double bond character of the C(6)–N(1) bond, which is consistent with the observation of two distinct NMe resonances in the ^1H- and ^{13}C-NMR spectra and emphasizes the importance of resonance form **J** (Scheme 6) for the description of the overall bonding situation in the binuclear complexes. The C(6)–C(7) distance is only slightly shorter than that of a C(sp^2)–C(sp) bond (1.431 Å)[20] and that in **1a** (1.434 Å)[5] which indicates that the importance of the resonance structure **K** increases only slightly when $SiMe_3$ is replaced by a transition metal ligand fragment. The same conclusion can be drawn from the similarity of the C≡C distance in the binuclear complexes with that in other ethynylcarbene complexes such as **1a** (1.196 Å)[5], [$(CO)_5Cr{=}C[N(Me)C_6H_{11}]C{\equiv}CH$] [1.181(5) Å][21], [$(CO)_5Cr{=}C(OEt)C{\equiv}CPh$] [1.19(3) Å][22], [$(CO)_5W{=}C(OMe)C{\equiv}C{-}Re(NO)(PPh_3)Cp^*$] [1.23(1) Å][2] or in the alkynyl complexes [$Cp(CO)_2FeC{\equiv}CPh$] [1.201(9) Å][23] and [$Cp(PPh_3)_2RuC{\equiv}CPh$] [1.215(4) Å][24]. These structural features, i.e. a short C(7)–C(8) bond, a rather long C(6)–C(7) bond and the strong mesomeric interaction between the amino nitrogen and the C(6) atom imply that a strong mesomeric interaction between the two metal centers in these binuclear complexes is absent.

The various binuclear complexes principally differ in the orientation of the ML_n fragment with respect to the $(CO)_5W{=}C(NMe_2)C{\equiv}C$ unit. In **4a**, the carbene plane [formed by the atoms C(6), N(1) and C(7)] and the "Ni" plane C(8), Ni(1), P(1) are skewed (angle between these planes: 119.3°). In **5a**, the Ni atom is nearly planar coordinated [Ni(1) and the Ni-bound atoms deviate only slightly from the mean plane through the NiC_2P_2 fragment [Ni(1): 0.00 Å, P(1) and P(2): −0.12 Å, C(8): +0.12 Å, C(31): +0.11 Å)]. The NiC_2P_2 plane and the carbene plane are almost orthogonal (angle between the planes: 93.2°). In contrast, in **7a** and in **10a**, the carbene plane and the mirror plane of the $Cp(CO)_2M$ fragment almost coincide [angle between these planes: 12.5° (M = Fe) and 14.6° (M = Ru); NMe_2 an Cp "*cis*"].

Conclusion

Our results demonstrate the feasibility of the concept coupling an $(L')_mM'C_3$ and an ML_n fragment for the synthesis of heterobimetallic complexes with a π-conjugated C_3 propynylidene chain. A wide range of bimetallic complexes are accessible, either by nucleophilic substitution of the halide X in [XML_n] by lithiated ethynylcarbene complexes, or by Pd-catalyzed coupling of stannylated ethynylcarbene complexes with [XML_n]. The two approaches are complementary; those complexes which cannot be prepared by the substitution route (Scheme 2) are obtainable by the coupling route (Schemes 4 and 5).

Compared to the coupling of an $(L')_mM'C_2$ unit with a CML_n unit by reaction of a lithiated alkynyl complex with [$OC{-}ML_n$], as proposed by Gladysz et al., these routes (Schemes 2, 4 and 5) offer some advantages. They are not restricted to carbonyl-containing transition metal complexes with a strongly electrophilic carbonyl carbon atom. Metal halides without a carbonyl coligand, which are accessible in great variety, as well as carbonyl-containing metal halides can be employed.

The IR and NMR spectra indicate that the mesomeric interaction between the two metal centers is rather small. The ML_n fragment in [$(CO)_5M'{=}C(NR_2)C{\equiv}CML_n$] acts as a weak π-donor. The mesomeric interaction increases with increasing π-donor properties of the ML_n fragment. However, the enhancement is rather small, presumably due to the influence of the strong π-donor substituent NRMe at the carbene carbon atom, and does not significantly alter the various distances in the M=C–C≡C fragment.

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 (J. T. Baker, silica gel for flash chromatography) was argon-saturated. The complexes **1a**, **b**[5], [$ClNi(PPh_3)Cp$][25], [$BrNi(PMe_2Ph)_2(Mes)$][26], [$IFe(CO)_2Cp$][27], [$ClRu(CO)_2Cp$][28], [$ClRu(PPh_3)_2Cp$][29], [$BrMn(CO)_5$][27], [$BrRe(CO)_5$][27] and [$Cl_2Pd(MeCN)_2$][30] as well as Bu_3SnNEt_2[31] were prepared according to literature procedures. For the synthesis of **2a**, **b** by desilylation of **1a**, **b** KF/THF/MeOH was used instead of Bu_4NF/H_2O[5]. $HC{\equiv}CSiMe_3$ was obtained from Acros, [$ClRh(CO)(PPh_3)_2$] and Bu_3SnCl were purchased from Aldrich. NMR: Bruker AC 250, Bruker WM 250 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. – IR: Biorad FTS 60. – MS: Finnigan MAT 312. – Elemental analyses: Heraeus CHN-O-RAPID.

Pentacarbonyl{3-[(η⁵-cyclopentadienyl)(triphenylphosphane)nickelio]-1-dimethylaminopropynylidene}tungsten (**4a**) *and -chromium* (**4b**): 5.00 mmol of *n*BuLi (3.13 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 5.00 mmol of **2a** (2.03 g) or **2b** (1.37 g) in 30 ml of THF. The yellow solution was stirred for 30 min at −80°C. Then, 5.00 mmol (2.11 g) of [$ClNi(PPh_3)Cp$] was added and the mixture was stirred for 30 min at room temp. The color of the solution changed to dark-green. The solvent was removed in vacuo. The dark-green residue was dissolved in 10 ml of Et_2O and chromatographed at −40°C on silica gel with pentane/Et_2O [3:2 (**4a**), 2:1 (**4b**)]. The green band containing **4a** or **4b** was eluted. Evaporation of the solvent in vacuo afforded complexes **4a**, **b** as green solids. Recrystallization from 25 ml of Et_2O/pentane [5:2 (**4a**), 4:1 (**4b**)] gave **4a**, **b** as green crystals.

4a: Yield: 3.16 g (80%, based on **2a**), m.p. 148°C (dec.). – IR (Et_2O): ν(CO) = 2060 cm^{-1} w, 1965 w, 1922 s, 1903 m; ν(C≡C) = 2039 cm^{-1} w. – ^1H NMR: δ = 2.34 (s, 3H, CH_3), 3.35 (s, 3H, CH_3), 5.27 (s, 5H, C_5H_5), 7.35–7.44 (m, 9H, C_6H_5), 7.62–7.70 (m, 6H, C_6H_5). – ^{13}C NMR: δ = 43.16, 50.36 (CH_3), 93.14 (C_5H_5), 128.34 [*J*(PC) = 10.5 Hz], 133.96 [*J*(PC) = 11.0 Hz] (*o*,*m*-C), 130.45 (*p*-C), 131.00 [^3J(PC) = 4.2 Hz, C_β], 133.26 [^1J(PC) n. f., *i*-C], 146.31 [^2J(PC) = 45.1 Hz, C_α], 199.68 [^1J(WC) = 127.9 Hz, *cis*-CO], 205.04 (*trans*-CO), 226.06 (W=C). – ^{31}P NMR: δ = 44.05. – MS (FAB, NBOH); *m/z* (%): 789 (30) [M^+ (^{184}W, ^{58}Ni)], 761 (28), 733 (52), 705 (100), 677 (53), 649 (49) [$M^+ - n$ CO, n = 1−5], 385 (88) [$Ni(C_5H_5)PPh_3^+$]. − $C_{33}H_{26}NNiO_5PW$ (790.1): calcd. C 50.17, H 3.32, N 1.77; found C 50.00, H 3.29, N 1.78.

4b: Yield: 2.63 g (80%, based on **2b**), m.p. 138 °C (dec.). − IR (Et_2O): ν(CO) = 2052 cm^{-1} w, 1968 w, 1925 s, 1905 m; ν(C≡C) = 2036 cm^{-1} w. − ^1H NMR: δ = 2.37 (s, 3H, CH_3), 3.41 (s, 3H, CH_3), 5.27 (s, 5H, C_5H_5), 7.33−7.46 (m, 9H, C_6H_5), 7.61−7.70 (m, 6H, C_6H_5). − ^{13}C NMR: δ = 44.67, 48.10 (CH_3), 93.13 (C_5H_5), 128.30 [J(PC) = 10.8 Hz], 133.93 [J(PC) = 11.2 Hz] (*o,m*-C), 129.53 [^3J(PC) = 3.2 Hz, C_β], 130.44 (*p*-C), 133.21 [^1J(PC) n. f., *i*-C], 148.44 [^2J(PC) = 46.3 Hz, C_α], 218.40 (*cis*-CO), 224.69 (*trans*-CO), 243.72 (Cr=C). − ^{31}P NMR: δ = 43.91. − $C_{33}H_{26}CrNNiO_5P$ (658.2): calcd. C 60.22, H 3.98, N 2.13; found C 60.12, H 4.03, N 2.23.

Pentacarbonyl{3-[trans-mesitylbis(dimethylphenylphosphane)-nickelio]-1-dimethylaminopropynylidene}tungsten (**5a**): 3.00 mmol of *n*BuLi (1.88 ml of a 1.6 M solution in hexane) was added to a solution of 3.00 mmol (1.22 g) of **2a** in 20 ml of Et_2O at −80 °C. On stirring for 30 min at −80 °C, the yellow solution turned cloudy. Then, 3.00 mmol (1.48 g) of [$BrNi(PMe_2Ph)_2(Mes)$] and 10 ml of THF were added and the dark-yellow solution was stirred for 30 min at room temp. The solvent was removed in vacuo, the brown-yellow residue was dissolved in 6 ml of CH_2Cl_2 and chromatographed at −40 °C on silica gel. With pentane/CH_2Cl_2 (3:1) the yellow band containing **5a** was eluted. Evaporation of the solvent in vacuo and recrystallization from 25 ml of pentane/CH_2Cl_2 (1:4) afforded **5a** as yellow crystals. Yield: 2.16 g (84%, based on **2a**), m.p. 107 °C (dec.). − IR (Et_2O): ν(CO) = 2058 cm^{-1} w, 1965 w, 1921 s, 1903 sh; ν(C≡C) = 2007 cm^{-1} w. − ^1H NMR (CD_2Cl_2, −40 °C): δ = 1.21 [t, ^2J(PH) = 3.7 Hz, 12H, PCH_3], 2.10 (s, 3H, *p*-CH_3), 2.17 (s, 6H, *o*-CH_3), 3.05 [s, 3H, N(CH_3)], 3.49 [s, 3H, N(CH_3)], 6.47 (s, 2H, *m*-H), 7.31−7.38 (m, 6H, PC_6H_5), 7.63−7.71 (m, 4H, PC_6H_5). − ^{13}C NMR ($CDCl_3$, −40 °C): δ = 14.41 [^1J(PC) = 15.8 Hz, PCH_3], 20.66 (*p*-CH_3), 25.16 (*o*-CH_3), 43.59, 50.66 (NCH_3), 125.76, 127.74, 129.22, 131.17 [J(PC) = 4.5 Hz] (*o,m,p*-C of C_6H_5, *m*-C of Mes), 130.45, 131.52 (*o,p*-C of Mes), 136.13 [J(PC) = 20.9 Hz], 142.09, 155.75 [J(PC) = 30.6 Hz] (*i*-C of Mes, *i*-C of C_6H_5, C_β), 179.33 [^2J(PC) = 31.8 Hz, C_α], 199.31 [^1J(WC) = 127.7 Hz, *cis*-CO], 204.90 [^1J(WC) = 132.6 Hz, *trans*-CO], 221.23 [^1J(WC) = 85.1 Hz, W=C]. − ^{31}P NMR (CD_2Cl_2, room temp.): δ = 1.04. − MS (70 eV); *m/z* (%): 857 (0.5) [M^+ (^{184}W, ^{58}Ni)], 801 (0.7) [M^+ − 2 CO], 745 (0.6) [M^+ − 4 CO], 717 (0.7) [M^+ − 5 CO], 579 (4) [M^+ − 5 CO − PMe_2Ph], 523 (4) [M^+ − $Ni(PMe_2Ph)_2$], 334 (100) [$Ni(PMe_2Ph)_2^+$], 196 (51) [$Ni(PMe_2Ph)^+$]. − $C_{35}H_{39}NNiO_5P_2W$ (858.2): calcd. C 48.99, H 4.58, N 1.63; found C 48.84, H 4.54, N 1.85.

Pentacarbonyl{3-[trans-carbonylbis(triphenylphosphane)rhodio]-1-dimethylaminopropynylidene}tungsten (**6a**): 1.00 mmol of *n*BuLi (0.63 ml of a 1.6 M solution in hexane) was added to a solution of 1.00 mmol (0.41 g) of **2a** in 10 ml of Et_2O at −80 °C. On stirring the yellow solution for 30 min at −80 °C, formation of a white precipitate was observed. Then, 1.00 mmol (0.69 g) of [$ClRh(CO)(PPh_3)_2$] and 5 ml of THF were added and the mixture was stirred for 30 min at room temp. The solvent was removed in vacuo. The residue was dissolved in 3 ml of CH_2Cl_2 and chromatographed at −40 °C with pentane/CH_2Cl_2 (3:2) on silica gel. A yellow band was eluted, evaporation of the solvent from which afforded complex **6a** as a yellow powder. Yield: 0.88 g (83%, based on **2a**), m.p. 146 °C (dec.). − IR (Et_2O): ν(CO) = 2059 cm^{-1} w, 1969 w, 1926 s, 1914 s, 1902 sh; ν(C≡C) = 1987 cm^{-1} m. − ^1H NMR: δ = 2.29 (s, 3H, CH_3), 3.22 (s, 3H, CH_3), 7.31−7.42 (m, 18H, C_6H_5), 7.67−7.75 (m, 12H, C_6H_5). − ^{13}C NMR: δ = 43.37, 50.52 (CH_3), 128.03 [J(PC) n. f.], 134.61 [J(PC) = 6.0 Hz] (*m,o*-C), 129.97 (*p*-C), 131.37 (C_β), 134.18 [^1J(PC) = 22.7 Hz, *i*-C], 175.27 [^1J(RhC) = 42.3 Hz, ^2J(PC) = 21.6 Hz, C_α], 193.85 (RhCO), 199.30 [^1J(WC) = 128.4 Hz, *cis*-WCO], 204.59 (*trans*-WCO), 222.33 [^1J(WC) = 86.7 Hz, W=C]. − ^{31}P NMR: δ = 33.45 [^1J(RhP) = 135.1 Hz]. − MS (FAB, NBOH); *m/z* (%): 1059 (8) [M^+ (^{184}W, ^{103}Rh)], 1003 (7) [M^+ − 2 CO], 947 (10) [M^+ − 4 CO], 891 (38) [M^+ − 6 CO], 655 (41) [$Rh(CO)(PPh_3)_2^+$], 627 (85) [$Rh(PPh_3)_2^+$]. − $C_{47}H_{36}NO_6P_2RhW$ (1059.5): calcd. C 53.28, H 3.42, N 1.32; found C 53.23, H 3.52, N 1.50.

Pentacarbonyl{3-[dicarbonyl(η⁵-cyclopentadienyl)ferrio]-1-dimethylaminopropynylidene}tungsten (**7a**) *and -chromium* (**7b**)

(A) *Synthesis by Nucleophile Substitution:* 8.00 mmol of *n*BuLi (5.00 ml of a 1.6 M solution in hexane) was added to a solution of 8.00 mmol of **2a** (3.24 g) or **2b** (2.19 g) in 30 ml of Et_2O. On stirring the yellow solution for 30 min at −80 °C, a white precipitate was formed. Then, 8.00 mmol (2.43 g) of [$IFe(CO)_2Cp$] and 20 ml of THF were added and the mixture was stirred for 30 min at room temp. After removal of the solvent in vacuo, the dark residue was dissolved in 16 ml of Et_2O and chromatographed at −40 °C on silica gel. With pentane/Et_2O [3:2 (**7a**), 4:3 (**7b**)] the yellow band containing **7a** or **7b** was eluted. Removal of the solvent in vacuo and recrystallization from 45 ml of Et_2O/pentane [4:1 (**7a**), 5:2 (**7b**)] gave yellow crystals.

(B) *Synthesis by Coupling Reaction:* A solution of 5.00 mmol of **9a** (3.47 g) or **9b** (2.81 g), 5.00 mmol (1.52 g) of [$IFe(CO)_2Cp$] and 0.5 mmol (0.13 g) of [$Cl_2Pd(MeCN)_2$] in 20 ml of toluene was stirred for 2 d at room temp. The color of the solution changed from yellow to dark-brown. After evaporation of the solvent in vacuo, the dark residue was dissolved in 10 ml of Et_2O and chromatographed with pentane/Et_2O [3:2 (**7a**), 4:3 (**7b**)] at −40 °C on silica gel. First, a narrow yellow band containing **9a** or **9b**, and then an intensely yellow band containing **7a** or **7b** was eluted. Evaporation of the solvent in vacuo gave yellow solids.

7a: Yield: Route (A): 3.95 g (85%, based on **2a**); route (B): 2.41 g (83%, based on **9a**), m.p. 114 °C (dec.). − IR (Et_2O): ν(CO) = 2065 cm^{-1} br. w, 2034 m, 2003 m, 1967 w, 1923 s, 1907 sh; ν(C≡C) = 2067 cm^{-1} w. − ^1H NMR: δ = 3.51 (s, 3H, CH_3), 3.66 (s, 3H, CH_3), 5.12 (s, 5H, C_5H_5). − ^{13}C NMR: δ = 44.26, 50.65 (CH_3), 85.54 (C_5H_5), 127.79 (C_β), 148.77 (C_α), 199.58 [^1J(WC) = 128.3 Hz, *cis*-WCO], 204.92 [^1J(WC) = 131.7 Hz, *trans*-WCO], 211.15 (FeCO), 227.59 [^1J(WC) = 86.7 Hz, W=C]. − MS (FAB, NBOH); *m/z* (%): 581 (62) [M^+ (^{184}W, ^{56}Fe)], 553 (48), 525 (41), 497 (100), 469 (41), 441 (21), 413 (27), 385 (20) [$M^+ - n$ CO, n = 1−7]. − $C_{17}H_{11}FeNO_7W$ (581.0): calcd. C 35.15, H 1.91, N 2.41; found C 35.04, H 1.95, N 2.49.

7b: Yield: Route (A): 2.80 g (78%, based on **2b**); route (B): 1.59 g (71%, based on **9b**), m.p. 112 °C (dec.). − IR (Et_2O): ν(CO) = 2054 cm^{-1} w, 2032 m, 2002 m, 1969 w, 1926 sw, 1910 sh; ν(C≡C) = 2066 cm^{-1} w. − ^1H NMR: δ = 3.54 (s, 3H, CH_3), 3.74 (s, 3H, CH_3), 5.13 (s, 5H, C_5H_5). − ^{13}C NMR: δ = 45.74, 48.40 (CH_3), 85.50 (C_5H_5), 126.38 (C_β), 150.93 (C_α), 211.15 (FeCO), 218.37 (*cis*-CrCO), 224.54 (*trans*-CrCO), 245.90 (Cr=C). − MS (70 eV); *m/z* (%): 449 (2) [M^+ (^{52}Cr, ^{56}Fe)], 393 (8), 365 (2), 337 (10), 309 (19), 281 (40), 253 (73), [$M^+ - n$ CO, n = 2−7]. − $C_{17}H_{11}CrFeNO_7$ (449.1): calcd. C 45.46, H 2.47, N 3.12; found C 45.54, H 2.48, N 3.27.

Pentacarbonyl{1-N-[dicarbonyl(η⁵-cyclopentadienyl)ferrio]methylamino-3-trimethylsilylpropynylidene}tungsten (**8a**): 4.00 mmol of MeLi · LiBr (2.67 ml of a 1.5 M solution in Et_2O) was added at −80 °C to a solution of 4.00 mmol (1.91 g) of **1a** in 80 ml of THF and the mixture was stirred at this temperature for 30 min. Then, 4.00 mmol (1.22 g) of [$IFe(CO)_2Cp$] was added. The brown solution was stirred for 30 min at room temp. and then the solvent was removed in vacuo. The brown residue was dissolved in 8 ml of CH_2Cl_2 and chromatographed with pentane/CH_2Cl_2 (3:2) at −30 °C on silica gel. First, a narrow yellow band containing **1a**, and then an intensely yellow band containing **8a** was eluted. Removal of the solvent in vacuo afforded **8a** as an analytically pure yellow powder. Yield: 0.46 g (24%, based on **1a**), m.p. 132 °C (dec.). – IR (Et_2O): ν(CO) = 2059 cm^{-1} w, 2043 m, 1999 m, 1965 w, 1922 s, 1904 m. – ^1H NMR (CD_2Cl_2, room temp.): δ = 0.33 (s, 9H, $SiCH_3$), 3.70 (s, 3H, NCH_3), 5.10 (s, 5H, C_5H_5). – ^{13}C NMR (CD_2Cl_2, room temp.): δ = −0.52 ($SiCH_3$), 67.28 (NCH_3), 87.23 (C_5H_5), 114.99 (C_β), 125.92 (C_α), 200.56 [^1J(WC) = 128.3 Hz, *cis*-WCO], 205.67 (*trans*-WCO), 212.03 [$Fe(CO)_2$], 241.42 (W=C). – MS (70 eV); *m/z* (%): 639 (3) [M^+ (^{184}W, ^{56}Fe)], 611 (0.7), 583 (3), 555 (6), 527 (6), 499 (2), 471 (32), 443 (24) [M^+ – *n* CO, *n* = 1–7], 121 (100) [$Fe(C_5H_5)^+$]. – $C_{19}H_{17}FeNO_7SiW$ (639.1): calcd. C 35.71, H 2.68, N 2.19; found C 35.98, H 2.73, N 2.46.

Pentacarbonyl[(1-dimethylamino-3-tributylstannyl)propynylidene]tungsten (**9a**) *and -chromium* (**9b**): 10.00 mmol of *n*BuLi (6.25 ml of a 1.6 M solution in hexane) was added at −80 °C to a solution of 10.00 mmol of **2a** (4.05 g) or **2b** (2.73 g) in 40 ml of Et_2O. On stirring the yellow solution for 30 min at −80 °C, a white solid precipitated. Then, 10.00 mmol (3.26 g) of Bu_3SnCl was added at −80 °C and the mixture was stirred for 45 min at room temp. After evaporation of the solvent in vacuo the residue was dissolved in 40 ml of pentane and chromatographed at −30 °C on silica gel. With pentane/CH_2Cl_2 (5:1) a yellow band containing **9a** or **9b** was eluted. Removal of the solvent in vacuo afforded complexes **9a, b** as analytically pure yellow oils.

9a: Yield: 5.48 g (79%, based on **2a**). – IR (pentane): ν(CO) = 2063 cm^{-1} w, 1974 w, 1937 s, 1931 s. – ^1H NMR: δ = 0.90 (t, *J* = 7.2 Hz, 9H, CH_2CH_3), 0.98–1.16 (m, 6H, $SnCH_2$), 1.23–1.45 (m, 6H, $SnCH_2CH_2$), 1.50–1.74 (m, 6H, CH_2CH_3), 3.58 (s, 3H, NCH_3), 3.74 (s, 3H, NCH_3). – ^{13}C NMR: δ = 11.32 [^1J(^{117}SnC, ^{119}SnC) = 379.0 Hz, 362.83 Hz, $SnCH_2$], 13.52 (CH_2CH_3), 26.92 [^2J($^{117/119}$SnC) = 59.5 Hz, $SnCH_2CH_2$], 28.86 [^3J($^{117/119}$SnC) = 24.1 Hz, CH_2CH_3], 45.82, 51.41 (NCH_3), 112.39 [^2J($^{117/119}$SnC) = 40.1 Hz, C_β], 136.07 [^1J(^{117}SnC, ^{119}SnC) = 249.1 Hz, 236.2 Hz, C_α], 198.68 [^1J(WC) = 127.0 Hz, *cis*-CO], 204.33 [^1J(WC) = 130.0 Hz, *trans*-CO], 230.28 [^1J(WC) = 87.6 Hz, W=C]. – MS (70 eV); *m/z* (%): 695 (32) [M^+ (^{184}W, ^{120}Sn)], 639 (81) [M^+ – 2 CO], 583 (39) [M^+ – 4 CO], 555 (41) [M^+ – 5 CO], 469 (17) [M^+ – 4 CO – 2 Bu], 441 (100) [M^+ – 5 CO – 2 Bu], 412 (49) [M^+ – 4 CO – 3 Bu], 385 (54) [M^+ – 5 CO – 2 Bu – C_4H_8]. – $C_{22}H_{33}NO_5SnW$ (694.1): calcd. C 38.07, H 4.79, N 2.02; found C 38.12, H 4.76, N 2.00.

9b: Yield: 4.55 g (81%, based on **2b**). – IR (pentane): ν(CO) = 2056 cm^{-1} w, 1977 w, 1941 s, 1935 s. – ^1H NMR: δ = 0.83–0.93 (m, 9H, CH_2CH_3), 1.06–1.12 (m, 6H, $SnCH_2$), 1.30–1.34 (m, 6H, $SnCH_2CH_2$), 1.35–1.62 (m, 6H, CH_2CH_3), 3.62 (s, 3H, NCH_3), 3.84 (s, 3H, NCH_3). – ^{13}C NMR: δ = 11.34 [^1J(^{117}SnC, ^{119}SnC) = 379.05 Hz, 363.03 Hz, $SnCH_2$], 13.58 (CH_2CH_3), 26.97 [^2J($^{117/119}$SnC) = 61.0 Hz, $SnCH_2CH_2$], 28.91 [^3J($^{117/119}$SnC) = 23.6 Hz, CH_2CH_3], 47.31, 49.26 (NCH_3), 110.73 [^2J($^{117/119}$SnC) = 41.6 Hz, C_β], 138.98 (C_α), 217.51 (*cis*-CO), 224.22 (*trans*-CO), 250.60 (Cr=C). – MS (70 eV); *m/z* (%): 563 (1) [M^+, (^{52}Cr, ^{120}Sn)], 507 (2), 479 (2), 451 (4), 423 (10) [M^+ – *n* CO, *n* = 2–5)], 309 (13) [M^+ – 5 CO – 2 Bu], 253 (46) [M^+ – 5 CO – 2 Bu – C_4H_8], 52 (100) [Cr^+]. – $C_{22}H_{33}CrNO_5Sn$ (562.2): calcd. C 47.00, H 5.92, N 2.49; found C 46.98, H 5.97, N 2.53.

Pentacarbonyl{3-[dicarbonyl(η⁵-cyclopentadienyl)ruthenio]-1-dimethylaminopropynylidene}tungsten (**10a**) *and -chromium* (**10b**): 3.00 mmol of **9a** (2.08 g) or **9b** (1.69 g), 3.00 mmol (0.77 g) of [$ClRu(CO)_2Cp$] and 0.30 mmol (0.08 g) of [$Cl_2Pd(MeCN)_2$] were dissolved in 15 ml of toluene. The solution was stirred for 1 d at room temp. The color changed from yellow to dark-brown. Removal of the solvent in vacuo afforded a dark-brown residue which was dissolved in 6 ml of CH_2Cl_2 and chromatographed at −30 °C on silica gel. With pentane/CH_2Cl_2 [1:1 (**10a**), 5:4 (**10b**)] the yellow band containing **10a** or **10b** was eluted. Evaporation of the solvent in vacuo and recrystallization from 25 ml of pentane/CH_2Cl_2 [1:3 (**10a**), 1:5 (**10b**)] gave yellow crystals.

10a: Yield: 1.16 g (62%, based on **9a**), m.p. 132 °C (dec.). – IR (Et_2O): ν(CO) = 2077 cm^{-1} w, 2039 m, 2004 m, 1967 w, 1923 s, 1906 sh; ν(C≡C) = 2062 cm^{-1} w. – ^1H NMR: δ = 3.54 (s, 3H, CH_3), 3.66 (s, 3H, CH_3), 5.51 (s, 5H, C_5H_5). – ^{13}C NMR: δ = 44.39, 50.67 (CH_3), 88.13 (C_5H_5), 121.67 (C_β), 140.66 (C_α), 195.72 (RuCO), 199.51 [^1J(WC) = 127.0 Hz, *cis*-WCO], 204.92 [^1J(WC) = 131.68 Hz, *trans*-WCO], 228.25 [^1J(WC) = 85.4 Hz, W=C]. – MS (70 eV); *m/z* (%): 627 (19) [M^+ (^{184}W, ^{102}Ru)], 599 (11), 571 (12), 543 (56), 515 (100), 487 (27), 459 (73), 431 (59) [M^+ – *n* CO, *n* = 1–7]. – $C_{17}H_{11}NO_7RuW$ (626.2): calcd. C 32.61, H 1.77, N 2.24; found C 32.71, H 1.73, N 2.44.

10b: Yield: 0.88 g (59%, based on **9b**), m.p. 127 °C (dec.). – IR (Et_2O): ν(CO) = 2075 cm^{-1} w, 2037 m, 2003 m, 1970 w, 1926 s, 1910 sh; ν(C≡C) = 2056 w. – ^1H NMR: δ = 3.58 (s, 3H, CH_3), 3.74 (s, 3H, CH_3), 5.52 (s, 5H, C_5H_5). – ^{13}C NMR: δ = 45.90, 48.45 (CH_3), 88.13 (C_5H_5), 120.29 (C_β), 142.91 (C_α), 195.77 (RuCO), 218.32 (*cis*-CrCO), 224.53 (*trans*-CrCO), 246.94 (Cr=C). – MS (70 eV); *m/z* (%): 495 (0.7) [M^+ (^{52}Cr, ^{102}Ru)], 467 (0.3), 439 (3), 411 (0.9), 383 (8), 355 (7), 327 (34), 299 (27) [M^+ – *n* CO, *n* = 1–7], 52 (100) [Cr^+]. – $C_{17}H_{11}CrNO_7Ru$ (494.3): calcd. C 41.30, H 2.24, N 2.83; found C 41.18, H 2.42, N 3.09.

Pentacarbonyl{3-[carbonyl(η⁵-cyclopentadienyl)(triphenylphosphane)ruthenio]-1-dimethylaminopropynylidene}tungsten (**11a**): A solution of 3.00 mmol (2.08 g) of **9a**, 3.00 mmol (2.18 g) of [$ClRu(PPh_3)_2Cp$] and 0.30 mmol (0.08 g) of [$Cl_2Pd(MeCN)_2$] in 15 ml of toluene was stirred for 3 d at room temp. The color changed from yellow to dark-brown. The solvent was removed in vacuo, the dark-brown residue was dissolved in 6 ml of CH_2Cl_2 and chromatographed with pentane/CH_2Cl_2 (3:2) at −30 °C on silica gel. A yellow band contained **11a**. Yield: 0.57 g (22%, based on **9a**), m.p. 158 °C (dec.). – IR (Et_2O): ν(CO) = 2060 cm^{-1} w, 1978 sh, 1963 m, 1919 s, 1902 sh; ν(C≡C) = 2035 cm^{-1} m. – ^1H NMR: δ = 2.81 (s, 3H, CH_3), 3.50 (s, 3H, CH_3), 5.09 (s, 5H, C_5H_5), 7.32–7.52 (m, 15H, C_6H_5). – ^{13}C NMR: δ = 43.44, 50.57 (CH_3), 87.89 (C_5H_5), 126.24 (C_β), 128.24 [*J*(PC) = 10.9 Hz], 133.47 [*J*(PC) = 11.2 Hz] (*m,o*-C), 130.26 (*p*-C), 135.65 [^1J(PC) = 49.9 Hz, *i*-C], 161.64 [^2J(PC) = 21.4, C_α], 199.98 [^1J(WC) = 127.2 Hz, *cis*-WCO], 202.96 [^2J(PC) = 18.6 Hz, RuCO], 204.94 [^1J(WC) = 131.7 Hz, *trans*-WCO], 225.11 [^1J(WC) = 85.1 Hz, W=C]. – ^{31}P NMR: δ = 55.80. – MS (FAB, NBOH); *m/z* (%): 861 (9) [M^+ (^{184}W, ^{102}Ru)], 833 (14), 805 (22), 777 (26), 749 (36), 721 (55), 693 (100) [M^+ – *n* CO, *n* = 1–6]. – $C_{34}H_{26}NO_6PRuW$ (860.5): calcd. C 47.46, H 3.05, N 1.63; found C 47.52, H 2.94, N 1.87.

Pentacarbonyl{3-[(pentacarbonyl)manganio]-1-dimethylaminopropynylidene}tungsten (**12a**) *and Pentacarbonyl{3-[(pentacarbonyl)rhenio]-1-dimethylaminopropynylidene}tungsten* (**13a**): A solution of 3.00 mmol (2.08 g) of **9a**, 3.00 mmol of $BrM(CO)_5$ [M = Mn (0.82 g) or Re (1.22 g)] and 0.30 mmol (0.08 g) of [$Cl_2Pd(MeCN)_2$] in 15 ml of toluene (M = Mn) or in 20 ml of toluene/THF (1:1) (M = Re) was stirred for 1 d at room temp. The solvent was then removed in vacuo, the dark-brown residue was dissolved in 6 ml of CH_2Cl_2 and chromatographed with pentane/CH_2Cl_2 (4:1) at −40 °C on silica gel. First, a pale-yellow band ([$W(CO)_6$]) was eluted. A second pale-yellow band afforded, after removal of the solvent in vacuo, complexes **12a** and **13a** as pale-yellow powders.

12a: Yield: 0.63 g (35%, based on **9a**), m.p. 120°C (dec.). – IR (Et$_2$O): ν(CO) = 2138 cm^{-1} w, 2062 w, 2046 m, 2019 w, 1927 s, 1911 sh; ν(C≡C) = 2080 cm^{-1} w. – ^{1}H NMR: δ = 3.56 (s, 3H, CH$_3$), 3.70 (s, 3H, CH$_3$). – ^{13}C NMR: δ = 44.85, 51.00 (CH$_3$), 125.04 (C$_\beta$), 144.15 (C$_\alpha$), 199.22 [^1J(WC) = 128.4 Hz, *cis*-WCO], 204.66 [*trans*-WCO], 205.68 [*cis*-MnCO], 207.63 [*trans*-MnCO], 229.33 [^1J(WC) = 86.7 Hz, W=C]. – MS (70 eV); *m*/*z* (%): 599 (18) [M$^+$ (^{184}W, ^{55}Mn)], 571 (8), 543 (11), 515 (7), 487 (3), 459 (17), 431 (38), 403 (100), 375 (29), 347 (25), 319 (18) [M$^+$ – *n* CO, *n* = 1–10]. – C$_{15}$H$_6$MnNO$_{10}$W (599.0): calcd. C 30.08, H 1.01, N 2.34; found C 30.06, H 1.08, N 2.31.

13a: Yield: 0.20 g (9%, based on **9a**), m.p. 131°C (dec.). – IR (Et$_2$O): ν(CO) = 2151 cm^{-1} w, 2062 w, 2041 m, 2004 w, 1926 s, 1909 sh; ν(C≡C) = 2082 cm^{-1} w. – ^{1}H NMR: δ = 3.54 (s, 3H, CH$_3$), 3.67 (s, 3H, CH$_3$). – ^{13}C NMR: δ = 44.95, 50.91 (CH$_3$), 120.27 (C$_\beta$), 132.63 (C$_\alpha$), 177.71 [*cis*-ReCO], 180.56 [*trans*-ReCO], 199.32 [^1J(WC) = 128.1 Hz, *cis*-WCO], 204.75 [^1J(WC) = 131.6 Hz, *trans*-WCO], 230.28 [^1J(WC) = 86.4 Hz, W=C]. – MS (70 eV); *m*/*z* (%): 731 (27) [M$^+$ (^{184}W, ^{187}Re)], 703 (15), 675 (17), 647 (60), 619 (100), 591 (81), 563 (64), 535 (49), 507 (50), 479 (37), 451 (26) [M$^+$ – *n* CO, *n* = 1–10], 407 (25) [M$^+$ – W(CO)$_5$]. – C$_{15}$H$_6$NO$_{10}$ReW (730.3): A correct elemental analysis of **11a** could not be obtained.

Pentacarbonyl[(1-methylamino-3-trimethylsilyl)propynylidene]tungsten (**14a**) *and -chromium* (**14b**): 28.3 mmol of *n*BuLi (17.7 ml of a 1.6 M solution in hexane) was added at −80°C to a solution of 28.3 mmol (2.78 g) of HC≡CSiMe$_3$ in 160 ml of Et$_2$O. After stirring the mixture for 30 min at 0°C, 28.3 mmol of [W(CO)$_6$] (9.96 g) or [Cr(CO)$_6$] (6.23 g) and 20 ml of THF were added. The solid [M(CO)$_6$] slowly dissolved within 1 h at room temp., and the color of the solution changed from light-yellow to dark-red. The red solution was cooled to 0°C and 42.5 mmol (6.97 g) of F$_3$CSO$_3$Me was added dropwise. The reaction mixture immediately turned brown. Stirring was continued for 15 min at 0°C. Then, the solution was cooled to −100°C and 56.6 mmol of H$_2$NMe (4.92 ml of a 40% aqueous solution) was added dropwise. The cold solution, which turned yellow, was extracted immediately with three 200-ml portions of a saturated aqueous NaHCO$_3$ solution. The yellow organic layers were combined and the solvent was evaporated in vacuo. The brown-yellow residue was dissolved in 100 ml of pentane and chromatographed at −40°C with pentane/CH$_2$Cl$_2$ (5:1) on silica gel. First, a pale-yellow band ([M(CO)$_6$]) was eluted. The following yellow band gave, after removal of the solvent in vacuo, complexes **14a**, **b** as analytically pure yellow powders.

14a: Yield: 11.2 g [83%, based on W(CO)$_6$], m.p. 71°C. – IR (pentane): ν(CO) = 2065 cm^{-1} w, 1977 w, 1945 s, 1932 sh, 1922 sh. – ^{1}H NMR: δ = 0.28 (s, 9H, SiCH$_3$), 3.28 (d, *J* = 5.1 Hz, 3H, NCH$_3$), 8.68 (br. s, 1H, NH). – ^{13}C NMR: δ = −0.73 (SiCH$_3$), 39.24 (NCH$_3$), 104.66 (C$_\beta$), 137.09 (C$_\alpha$), 198.25 [^1J(WC) = 128.3 Hz, *cis*-CO], 203.72 [^1J(WC) = 129.0 Hz, *trans*-CO], 235.73 [^1J(WC) = 85.3 Hz, W=C]. – MS (70 eV); *m*/*z* (%): 463 (22) [M$^+$ (^{184}W, ^{28}Si)], 407 (49), 379 (42), 351 (66), 323 (100) [M$^+$ – *n* CO, *n* = 2–5]. – C$_{12}$H$_{13}$NO$_5$SiW (463.2): calcd. C 31.12, H 2.83, N 3.02; found C 31.07, H 2.81, N 2.99.

14b: Yield: 7.87 g [82%, based on Cr(CO)$_6$], m.p. 47°C. – IR (pentane): ν(CO) = 2058 cm^{-1} w, 1982 w, 1949 s, 1940 sh, 1924 sh. – ^{1}H NMR: δ = 0.29 (s, 9H, SiCH$_3$), 3.38 (d, *J* = 5.0 Hz, 3H, NCH$_3$), 8.77 (br. s, 1H, NH). – ^{13}C NMR: δ = −0.71 (SiCH$_3$), 39.54 (NCH$_3$), 102.31 (C$_\beta$), 140.71 (C$_\alpha$), 217.05 (*cis*-CO), 223.41 (*trans*-CO), 259.71 (Cr=C). – MS (70 eV); *m*/*z* (%): 331 (4) [M$^+$ (^{52}Cr, ^{28}Si)], 275 (3), 247 (5), 219 (76), 191 (100) [M$^+$ – *n* CO, *n* = 2–5]. – C$_{12}$H$_{13}$CrNO$_5$Si (331.3): calcd. C 43.50, H 3.95, N 4.23; found C 43.60, H 4.04, N 4.26.

Pentacarbonyl[(1-methylamino)propynylidene]tungsten (**15a**) *and -chromium* (**15b**): 3.44 mmol (0.20 g) of KF was added to a solution of 15.00 mmol of **14a** (6.95 g) or **14b** (4.97 g) in 80 ml of THF/MeOH (1:1) and the mixture was stirred for 10 min at room temp. Then, 200 ml of CH$_2$Cl$_2$ was added and the yellow solution was extracted with three 150 ml portions of a saturated aqueous NaHCO$_3$ solution. The yellow organic layers were combined and the solvent was evaporated in vacuo. The yellow residue was dissolved in 60 ml of pentane and chromatographed at −40°C on silica gel with pentane/CH$_2$Cl$_2$ [5:1 (**15a**), 4:1 (**15b**)]. The yellow band was collected. Removal of the solvent afforded **15a**, **b** as analytically pure yellow powders.

15a: Yield: 3.81 g (65%, based on **14a**), m.p. 90°C (dec.). – IR (pentane): ν(CO) = 2066 cm^{-1} w, 1976 w, 1939 s, 1926 sh. – ^{1}H NMR: δ = 3.32 (d, *J* = 5.1 Hz, 3H, NCH$_3$), 5.70 (s, 1H, C≡CH), 8.87 (br. s, 1H, NH). – ^{13}C NMR: δ = 39.44 (NCH$_3$), 84.58 (C$_\beta$), 114.72 (C$_\alpha$), 198.00 [^1J(WC) = 127.0 Hz, *cis*-CO], 203.51 [^1J(WC) = 128.6 Hz, *trans*-CO], 236.00 [^1J(WC) = 86.8 Hz, W=C]. – MS (70 eV); *m*/*z* (%): 391 (33) [M$^+$ (^{184}W)], 335 (31), 307 (57), 279 (95), 251 (100) [M$^+$ – *n* CO, *n* = 2–5]. – C$_9$H$_5$NO$_5$W (391.0): calcd. C 27.65, H 1.29, N 3.58; found C 27.61, H 1.33, N 3.55.

15b: Yield: 2.45 g (63%, based on **14b**), m.p. 84°C (dec.). – IR (pentane): ν(CO) = 2060 cm^{-1} w, 1986 w, 1952 s, 1929 sh. – ^{1}H NMR: δ = 3.42 (d, *J* = 4.9 Hz, 3H, NCH$_3$), 5.97 (s, 1H, C≡CH), 8.96 (br. s, 1H, NH). – ^{13}C NMR: δ = 39.67 (NCH$_3$), 82.28 (C$_\beta$), 118.22 (C$_\alpha$), 216.79 (*cis*-CO), 223.18 (*trans*-CO), 260.26 (Cr=C). – MS (70 eV); *m*/*z* (%): 259 (8) [M$^+$ (^{52}Cr)], 203 (4), 175 (10), 147 (19), 119 (93) [M$^+$ – *n* CO, *n* = 2–5], 52 (100) [Cr$^+$]. – C$_9$H$_5$CrNO$_5$ (259.1): calcd. C 41.71, H 1.94, N 5.41; found C 41.72, H 2.04, N 5.39.

Pentacarbonyl[(1-methylamino-3-tributylstannyl)]propynylidene]tungsten (**16a**) *and -chromium* (**16b**): A solution of 5.00 mmol of **15a** (1.96 g) or **15b** (1.30 g) and 5.00 mmol (1.81 g) of Bu$_3$SnNEt$_2$ in 20 ml of toluene was stirred for 30 min at room temp. Then, the solvent was removed in vacuo, the yellow residue was dissolved in 20 ml of pentane and chromatographed on silica gel at −30°C. With pentane/CH$_2$Cl$_2$ (5:1) a yellow band containing **16a** or **16b** was eluted. After removal of the solvent in vacuo, complexes **16a**, **b** were obtained as analytically pure yellow oils.

16a: Yield: 0.71 g (21%, based on **15a**). – IR (pentane): ν(CO) = 2064 cm^{-1} w, 1975 w, 1942 s, 1920 sh. – ^{1}H NMR: δ = 0.91 (t, *J* = 7.2 Hz, 9H, CH$_2$C*H*$_3$), 1.08–1.14 (m, 6H, SnCH$_2$), 1.28–1.42 (m, 6H, SnCH$_2$C*H*$_2$), 1.54–1.66 (m, 6H, C*H*$_2$CH$_3$), 3.28 (d, *J* = 5.0 Hz, 3H, NCH$_3$), 8.61 (br. s, 1H, NH). – ^{13}C NMR: δ = 11.47 [^1J(^{119}SnC, ^{117}SnC) = 377.5 Hz, 361.37 Hz, SnCH$_2$], 13.56 (CH$_2$CH$_3$), 26.90 [^2J($^{117/119}$SnC) = 59.2 Hz, SnCH$_2$*C*H$_2$], 28.86 [^3J($^{117/119}$SnC) = 24.7 Hz, *C*H$_2$CH$_3$], 38.80 (NCH$_3$), 111.04 [^2J($^{117/119}$SnC) = 36.8 Hz, C$_\beta$], 139.90 [^1J(^{119}SnC, ^{117}SnC) = 231.3 Hz, 221.7 Hz, C$_\alpha$], 198.53 [^1J(WC) = 127.0 Hz, *cis*-CO], 203.80 [^1J(WC) = 130.0 Hz, *trans*-CO], 235.27 [^1J(WC) = 85.5 Hz, W=C]. – MS (70 eV); *m*/*z* (%): 681 (24) [M$^+$ (^{184}W, ^{120}Sn)], 625 (50) [M$^+$ – 2 CO], 569 (22) [M$^+$ – 4 CO], 541 (57) [M$^+$ – 5 CO], 427 (100) [M$^+$ – 4 CO – 2 Bu], 398 (40) [M$^+$ – 5 CO – 2 Bu], 371 (29) [M$^+$ – 5 CO – 2 Bu – C$_4$H$_8$]. – C$_{21}$H$_{31}$NO$_5$SnW (680.0): calcd. C 37.09, H 4.59, N 2.06; found C 37.24, H 4.68, N 2.23.

16b: Yield: 0.38 g (14%, based on **15b**). – IR (pentane): ν(CO) = 2056 cm^{-1} w, 1980 w, 1946 s, 1921 sh. – ^{1}H NMR: δ = 0.91 (t, *J* = 7.2 Hz, 9H, CH$_2$C*H*$_3$), 0.97–1.18 (m, 6H, SnCH$_2$), 1.28–1.48 (m, 6H, SnCH$_2$C*H*$_2$), 1.54–1.66 (m, 6H, C*H*$_2$CH$_3$), 3.37 (d, *J* = 5.0 Hz, 3H, NCH$_3$), 8.72 (br. s, 1H, NH). – ^{13}C NMR: δ = 11.47 [^1J(^{119}SnC, ^{117}SnC) = 378.9 Hz, 361.7 Hz, SnCH$_2$], 13.57

Table 1. Crystallographic data for **4a**, **5a**, **7a** and **10a**

	4a	**5a**	**7a**	**10a**
Empirical formula	$C_{33}H_{26}NNiO_5PW$	$C_{35}H_{39}NNiO_5P_2W$	$C_{17}H_{11}FeNO_7W$	$C_{17}H_{11}NO_7RuW$
Formula mass	790.1	858.2	581.0	626.2
Crystal size [mm^3]	0.3 x 0.3 x 0.3	0.3 x 0.3 x 0.3	0.3 x 0.3 x 0.3	0.25 x 0.25 x 0.25
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a [Å]	12.833(1)	9.133(3)	11.126(1)	11.233(1)
b [Å]	16.379(1)	11.936(3)	8.832(1)	8.833(1)
c [Å]	15.951(1)	17.711(5)	19.154(2)	19.191(2)
α [deg]		81.00(1)		
β [deg]	109.69(1)	75.58(1)	97.75(1)	96.15(1)
γ [deg]		74.58(2)		
V [Å^3]	3156.7(4)	1798.2(9)	1865.9(3)	1893.5(3)
Z	4	2	4	4
Density [g·cm^{-3}]	1.662	1.585	2.068	2.197
Temperature [K]	244	216	236	217
Absorption [mm^{-1}]	4.408	3.918	7.109	7.022
Min/max transm	0.2433/0.2962	0.3444/0.5817	0.0756/0.1442	0.1052/0.1386
Indepdt reflns	6888	7859	4077	4140
Obsd reflns ($F > 4\sigma(F)$)	5086	6795	3248	3398
F(000)	1552	856	1104	1176
Index range	+16, +20, ±20	+11, ±15, ±22	+14, +11, ±24	+14, +11, ±24
Params refined	379	406	244	244
Final R	0.0372	0.0301	0.0333	0.0341
Final R_w	0.0407	0.0335	0.0362	0.0371
Largest diff peak/hole [e·Å^{-3}]	+1.07/-0.58	+1.00/-0.93	+1.16/-1.34	+0.84/-0.79

($SnCH_2CH_3$), 26.92 [$^2J(^{117/119}SnC)$ = 59.1 Hz, $SnCH_2CH_2$], 28.89 [$^3J(^{117/119}SnC)$ = 24.6 Hz, CH_2CH_3], 39.10 (NCH_3), 108.79 [$^2J(^{117/119}SnC)$ = 37.9 Hz, C_β], 142.97 [$^1J(^{117/119}SnC)$ = 229.7, C_α], 217.33 (*cis*-CO), 223.57 (*trans*-CO), 258.53 (Cr=C). – MS (70 eV); *m/z* (%): 549 (7) [M^+ (^{52}Cr, ^{120}Sn)], 493 (10), 465 (4), 437 (12), 409 (41) [M^+ – *n* CO, *n* = 2–5], 295 (35) [M^+ – 5 CO – 2 Bu], 239 (100) [M^+ – 5 CO – 2 Bu – C_4H_8], 52 (100) [Cr^+]. – $C_{21}H_{31}CrNO_5Sn$ (548.2): calcd. C 46.01, H 5.70, N 2.56; found C 46.11, H 5.85, N 2.50.

Pentacarbonyl{3-[dicarbonyl(η^5-cyclopentadienyl)ferrio]-1-methylaminopropynylidene}tungsten (**17a**) *and -chromium* (**17b**): A solution of 3.00 mmol of **16a** (2.04 g) or **16b** (1.65 g), 3.00 mmol (0.91 g) of [$IFe(CO)_2Cp$] and 0.30 mmol (0.08 g) of [$Cl_2Pd(MeCN)_2$] in 10 ml of toluene was stirred for 2 d at room temp. Then, the solvent of the dark-brown solution was evaporated in vacuo, the residue was dissolved in 6 ml of Et_2O and chromatographed with pentane/Et_2O [5:3 (**17a**), 3:2 (**17b**)] at –40 °C on silica gel. First, a narrow yellow band containing **16a** or **16b**, and then an intensely yellow band containing **17a** or **17b** was eluted. Removal of the solvent in vacuo afforded complexes **17a**, **b** as analytically pure yellow solids.

17a: Yield: 1.38 g (81%, based on **16a**), m.p. 105 °C (dec.). – IR (Et_2O): ν(CO) = 2068 cm^{-1} w, 2034 m, 2003 m, 1967 w, 1922 s, 1906 sh; ν(C≡C) = 2062 cm^{-1} w. – ^1H NMR: δ = 3.21 (d, *J* = 4.8 Hz, 3H, NCH_3), 5.13 (s, 5H, C_5H_5), 8.07 (br. s, 1H, NH). – ^{13}C NMR: δ = 37.36 (NCH_3), 85.73 (C_5H_5), 126.52 (C_β), 156.66 (C_α), 199.57 [^1J(WC) = 127.1 Hz, *cis*-WCO], 204.35 (*trans*-WCO), 210.91 [FeCO], 231.51 [^1J(WC) = 83.5 Hz, W=C]. – MS (70 eV); *m/z* (%): 567 (21) [M^+ (^{184}W, ^{56}Fe)], 539 (13), 511 (12), 483 (30), 455 (23), 427 (49), 399 (100), 371 (68) [M^+ – *n* CO, *n* = 1–7]. – $C_{16}H_9FeNO_7W$ (567.0): calcd. C 33.90, H 1.60, N 2.47; found C 33.88, H 1.80, N 2.67.

17b: Yield: 0.89 g (68%, based on **16b**), m.p. 105 °C (dec.). – IR (Et_2O): ν(CO) = 2068 cm^{-1} w, 2033 m, 2003 m, 1969 w, 1926 s, 1908 sh; ν(C≡C) = 2055 cm^{-1} w. – ^1H NMR ($CDCl_3$, –40 °C): δ = 3.32 (d, *J* = 3.4 Hz, 3H, NCH_3), 5.20 (s, 5H, C_5H_5), 8.26 (br. s, 1H, NH). – ^{13}C NMR: δ = 37.73 (NCH_3), 85.71 (C_5H_5), 124.37 (C_β), 159.44 (C_α), 210.94 (FeCO), 218.37 (*cis*-CrCO), 223.97 (*trans*-CrCO), 252.50 (Cr=C). – MS (70 eV); *m/z* (%): 435 (2) [M^+ (^{52}Cr, ^{56}Fe)], 407 (0.4), 379 (5), 351 (1), 323 (8), 295 (16), 267 (36), 239 (61) [M^+ – *n* CO, *n* = 1–7], 121 (26) [$Fe(C_5H_5)^+$], 52 (100) [Cr^+]. – $C_{16}H_9CrFeNO_7$ (435.1): calcd. C 44.17, H 2.08, N 3.22; found C 44.07, H 2.14, N 3.27.

X-ray Structural Analyses of **4a**, **5a**, **7a** *and* **10a**: Single crystals were grown from pentane/Et_2O [2:5 (**4a**), 1:4 (**7a**)] or pentane/CH_2Cl_2 [1:4 (**5a**), 1:3 (**10a**)], 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, 4–30° min^{-1} in ω) with a graphite monochromator ($Mo\text{-}K_\alpha$, 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[32].

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