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Intermetallic Communication through Carbon Wires in Heterobinuclear Cationic Allenylidene Complexes of Chromium

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The reaction of $[(CO)_5M(THF)]$ (M = Cr, W) with lithiated 2-ethynylquinoline followed by alkylation of the resulting alkynylpentacarbonylmetalate with $[R_3O]BF_4$ (R = Me, Et) gives allenylidene complexes in which the terminal carbon atom of the allenylidene chain is part of an N-alkylated quinoline ring. The reaction of $[(CO)_5M(THF)]$ (M = Cr, W) with lithiated 2-ethynylpyridine derivatives, $Li[C{\equiv}CC_5H_4BrN]$, and $[Et_3O]BF_4$ affords allenylidene complexes that contain a terminal six-membered N-heterocycle brominated at the 5- or 6-position. Various alkynyl groups can be introduced into the 5-position of the ring through $[PdCl_2(PPh_3)_2]$-catalyzed coupling of the 5-bromo-substituted allenylidene complexes with the terminal alkynes $HC{\equiv}CR'$ (R′ = TMS, Ph, $C_{10}H_{21}$, 4-C_6H_4-$C{\equiv}CPh$, 4-C_6H_4-$C{\equiv}CH$, Fc (Fc = $(C_5H_4)FeCp$), 4-C_6H_4-$C{\equiv}CFc$, 4-C_6H_4-$C{\equiv}CC_6H_4C{\equiv}CFc$). The analogous replacement reaction of the 6-bromo-substituted chromium complex with $HC{\equiv}CFc$ yields the corresponding 6-ferrocenylalkynyl-substituted complex. Desilylation of $[(CO)_5Cr{=}C{=}C{=}\overline{C(CH)_2C(C{\equiv}CSiMe_3)CHN}Et]$ (**6a**) gives $[(CO)_5Cr{=}C{=}C{=}\overline{C(CH)_2C(C{\equiv}CH)CHN}Et]$ (**15a**). CuI-catalyzed coupling of **15a** with {M}−Br ({M} = $Ru(CO)_2Cp$, $Fe(CO)_2Cp^*$) affords the binuclear complexes $[(CO)_5Cr{=}C{=}C{=}\overline{C(CH)_2C(C{\equiv}C{-}\{M\})CHN}Et]$. The symmetrical binuclear complex is formed by oxidative coupling of **15a** with $[Cu(OAc)_2]$. The attachment of a ferrocenyl group to the chromium center via PPh_2 to give *cis*-$[(CO)_4(Ph_2PFc)Cr{=}C{=}C{=}\overline{C(CH)_4N}Et]$ is achieved via displacement of a cis-CO ligand in $[(CO)_5Cr{=}C{=}C{=}\overline{C(CH)_4N}Et]$ by PPh_2Fc. On addition of $Co_2(CO)_8$ to $[(CO)_5Cr{=}C{=}C{=}\overline{C(CH)_2C(C{\equiv}CPh)CHN}Et]$ a $Co_2(CO)_6$ unit adds to the $C{\equiv}C$ bond to form a trinuclear complex. The ferrocenyl unit in $[(CO)_5Cr{=}C{=}C{=}\overline{C(CH)_2C(C{\equiv}CR)CHN}Et]$ (R = Fc, $C_6H_4C{\equiv}CFc$, $C_6H_4C{\equiv}CC_6H_4C{\equiv}CFc$) is readily oxidized. Spectroelectrochemical studies (IR, UV/vis) confirm that in the oxidized form there is strong electronic communication of the ferrocenyl group with the $(CO)_5Cr$ unit.

Introduction

Di- or oligonuclear transition-metal complexes with π-conjugated bridges are gaining considerable attention due to their versatile structural, chemical, and physicochemical properties. Organometallic push−pull systems with linear conjugated π-spacers have been proposed as a new class of one-dimensional wires[1] and exhibit both liquid crystalline[2] and NLO properties.[3] The electronic communication in polynuclear systems[4] is of particular interest, as it can be regarded as a model for a variety of comparable processes in biological systems[5] as well as in photonic[6] and electronic devices.[7] The properties of such complexes are determined by the usually redox-active terminal end groups and the type and length of the spacers. Most of the relevant work in this field relates to the investigation of mono- and polynuclear metal acetylides containing terminating orga-

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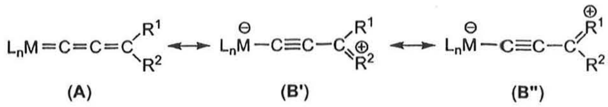
nometallic groups, such as $MnI(dmpe)_2$,[8] $Re(NO)(PPh_3)Cp^*$,[9] $Fe(CO)_2Cp^*$,[10] $Fe(dppe)Cp^*$,[11] $Fe(dippe)Cp^*$,[11] $Ru(dppe)Cp^*$,[12] $Ru(dppm)Cp^*$,[12] $Ru(PR_3)_2Cp^*$,[12] and similar systems[13] that offer the opportunity for single- or multi-electron-transfer processes. Additionally, bis(vinylidene)-, mixed vinylidene–alkynyl, and related highly conjugated complexes have been synthesized and investigated.

Scheme 1



In contrast, there have only been a few reports on electrochemical studies involving allenylidene complexes.[14] These investigations reveal that the site of oxidation is the metal center, thus increasing its acceptor properties. This leads to an enhanced alkynyl character of the cumulenylidene ligand (**B′** and **B″**, Scheme 1). Conversely, reduction mainly involves the allenylidene ligand, giving rise to an increased contribution of the cumulene-like resonance form to the overall bond description (**A**, Scheme 1).

This agrees well with the results of quantum chemical investigations.[15] These studies indicate that the HOMO is mainly localized at the metal center and the LUMO is delocalized within the carbon-rich ligand. One-electron reduction of $[Cl(dppe)_2Ru{=}C{=}C{=}CR_2]PF_6$ (R = Ph, Me) was observed to provide radical species with the unpaired electron localized on the cumulene moiety.[14i] Attaching an electroactive species such as a ferrocenyl unit to the terminal (sp^2-hybridized) carbon atom of the allenylidene ligand or to the central metal provides additional opportunities for influencing the electronic properties of the cumulene moiety.[14g,h]

We recently reported on a convenient one-pot synthesis of π-donor-substituted allenylidene complexes by reaction of readily available metal precursors with appropriate alkynes as the C_3 source.[16] The versatile chemistry of allenylidene complexes allows for the transformation of metallacumulenes into various other complexes such as heterocyclic carbene complexes.[17]

We now report on (a) the introduction of redox-active substituents or ligands into π-donor-substituted allenylidene complexes, (b) the synthesis of bi- or trinuclear allenylidene

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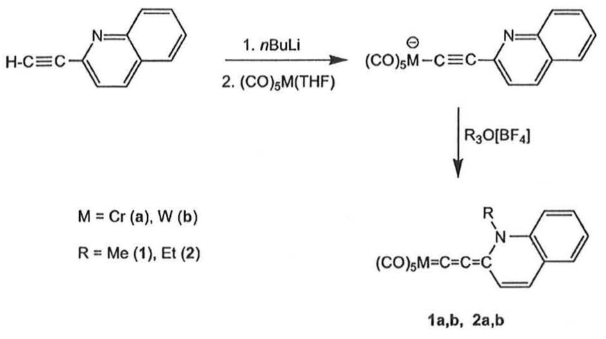
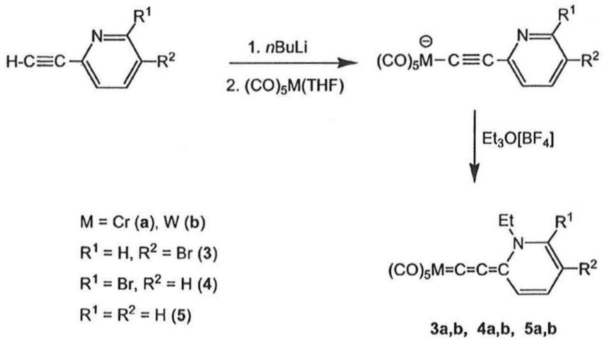
Scheme 2



M = Cr (a), W (b)
R = Me (1), Et (2)
1a,b, 2a,b

Scheme 3



M = Cr (a), W (b)
R^1 = H, R^2 = Br (3)
R^1 = Br, R^2 = H (4)
R^1 = R^2 = H (5)
3a,b, 4a,b, 5a,b

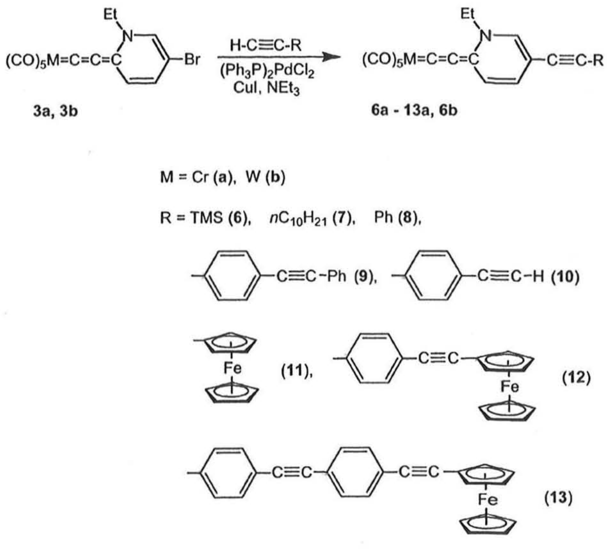
complexes containing different metal entities and various π-spacers, (c) the synthesis of a linear homobinuclear bis(allenylidene) complex by oxidative coupling of an ethynyl-substituted allenylidene complex, and (d) the spectroelectrochemical properties of some of these complexes.

Results and Discussion

Synthesis of N-Heterocyclic Allenylidene Complexes 1−4. The new allenylidene complexes **1**−**4** were prepared by following the synthetic protocol reported recently.[16] Reaction of the THF complexes [$(CO)_5M(THF)$] (M = Cr, W) with deprotonated 2-ethynylpyridines (2-ethinylquinoline) gave alkynylmetalates by displacement of the coordinated THF molecule. These alkynyl complexes were not isolated but were immediately alkylated with oxonium salts, $R_3O[BF_4]$ (R = Me, Et). After chromatography, the complexes **1a,b** and **2a,b** (Scheme 2) were obtained as deep violet solids in 68−80% yield. The corresponding bromo-functionalized complexes **3a,b** and **4a,b** (Scheme 3) were obtained as red solids in only moderate yields of 16−36%. In addition, the allenylidene complexes **5a,b**[16] were isolated in low yields (<20%) as byproducts in the synthesis of **3a,b** and **4a,b**. The formation of **5a,b** is readily explained by further lithiation of the lithium alkynyl precursor and subsequent protonation on silica. By deprotonation of 5-bromo-2-ethynylpyridine and 6-bromo-2-ethynylpyridine at −100 °C instead of at −78 °C, the halide/metal exchange could be minimized and the bromo-functionalized allenylidene complexes **3a,b** and **4a,b** were obtained in 20−47% yield (isolated yield of **5a,b** <5%).

Coupling of 3 and 4 with Terminal Alkynes. When **3a** was treated with an excess of (trimethylsilyl)ethyne (10 equiv) in the presence of catalytic amounts of $(PPh_3)_2PdCl_2$ (0.05 equiv), CuI (0.1 equiv), and triethylamine, complex **3a** was smoothly transformed into allenylidene complex **6a** within about 30 min. Complex **6a** was obtained, after chromatography, as a red solid in nearly quantitative yield. Other alkynyl substituents such as dodecynyl, phenylethynyl, and 4-alkynyl-substituted phenylethynyl groups could be introduced into the 5-position of the heterocycle as well. The corresponding mononuclear complexes **7a**−**10a** and **6b** were obtained in good to excellent yields (Scheme 4) by following the same procedure. The yields and the reaction times required for a complete conversion strongly depended on the excess of the terminal alkyne. The reaction rates significantly increased with increasing excess of the alkyne. Conversely, increasing the temperature led to lower yields, due to decomposition of the product complexes. When (trimethylsilyl)ethyne was used, the amount of the catalyst could be reduced to 0.01 equiv without loss of activity. Thus, an extension of the unsaturated chain can easily be accomplished and various terminating groups can be introduced into allenylidene complexes.

Scheme 4

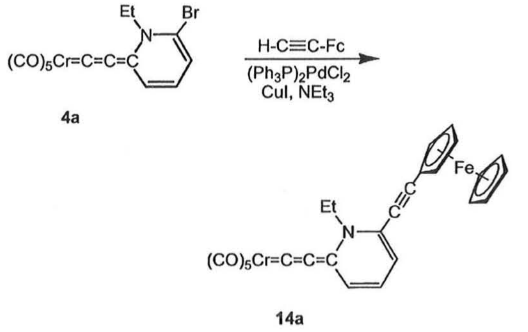


Ferrocene could likewise be attached to the terminating N-heterocycle of the allenylidene ligand through different unsaturated spacers by Pd/Cu-catalyzed coupling of **3a** with appropriate alkynyl-functionalized ferrocenes (Scheme 4). The complexes **11a**−**13a** were obtained in yields ranging from 45% (**13a**) to 73% (**11a**). In a pure form and under an inert atmosphere the complexes were stable at room temperature. However, under the conditions used in the synthesis of **6a**−**13a**, complex **13a** slowly decomposed. Therefore, the reactions were stopped after 60 min to avoid excessive decomposition of the product, thus explaining the rather low yield.

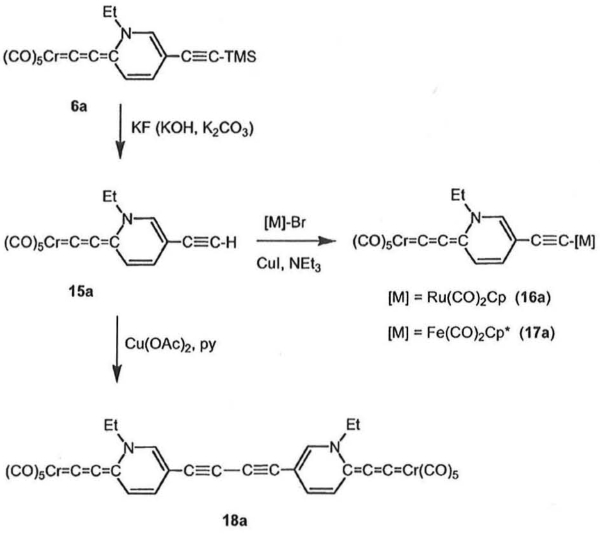
The 3-ethynylferrocene-substituted complex **14a**, analogous to **11a**, was prepared similarly by Pd/Cu-catalyzed coupling of ethynylferrocene with complex **4a** (Scheme 5).

Desilylation of complex **6a** to give the ethynyl-terminated derivative **15a** was achieved by treating solutions of **6a** in methanol at 0 °C with KF, KOH, or K_2CO_3 (Scheme 6). Complex **15a** was obtained, after chromatography, as a red solid in nearly quantitative yield. When complex **15a** was treated with a slight excess of copper(II) acetate (1.2 equiv) in the presence of pyridine, the *homo*binuclear bis(allenylidene) complex **18a** (Scheme 6) was formed. Compound **18a** was isolated after chromatography as violet oil in good yield. *Hetero*binuclear complexes were accessible by copper(I)-catalyzed coupling of **15a** with [$Cp(CO)_2Ru-Br$] and [$Cp^*(CO)_2Fe-Br$]. The heterobinuclear allenylidene−alkynyl complexes **16a** and **17a** (Scheme 6) were obtained in 58% and 38% yields, respectively.

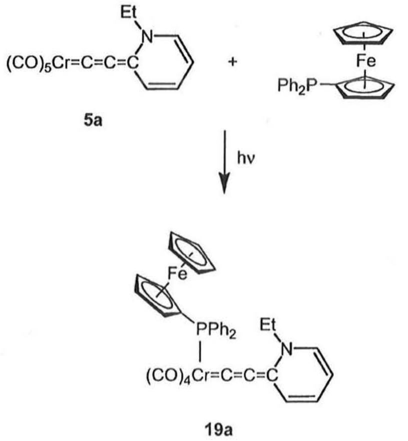
Scheme 5



Scheme 6



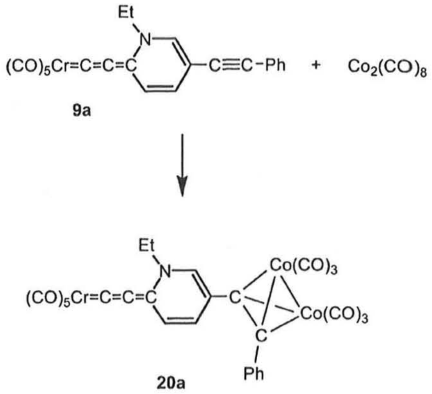
Scheme 7



The redox-active phosphine FcPh$_2$P could be introduced into the metal−ligand moiety via photolytically induced substitution. When **5a** was irradiated in the presence of a slight excess of ferrocenyldiphenylphosphine, the deep violet allenylidene complex **19a** was formed within about 2 h. Chromatography on silica afforded **19a** as a violet solid in 62% yield (Scheme 7).

Finally, the reaction of the phenylethynyl-terminated complex **9a** with a slight excess of octacarbonyldicobalt(0) at ambient temperature yielded (ca. 58%) the heterotrinuclear complex **20a** as a brown-violet oil (Scheme 8). The addition of the Co$_2$(CO)$_6$ fragment to the terminal C−C triple bond as well as to the C_α−C_β bond of the allenylidene ligand is conceivable, due to a considerable contribution of the zwitterionic alkynyl complex resonance forms **B′** and **B″** (see Scheme 1) to the overall bonding description. However, the reaction is highly regioselective. Only the product of coordination to the terminal C−C bond has been observed. There is no indication for complexation of the C_α−C_β bond. When the unsubstituted complex **5a** instead of **9a** was treated with Co$_2$(CO)$_8$ employing the same reaction conditions, complex **5a** rapidly decomposed. In contrast, in the absence of Co$_2$(CO)$_8$ complex **5a** is stable. These observations indicate that Co$_2$(CO)$_8$ (or a fragment derived from Co$_2$(CO)$_8$ by loss of CO) indeed interacts with the C_α−C_β bond. However, the product of such an interaction is unstable and rapidly decomposes. The rapid decomposition on complexation of the C_α−C_β bond is presumably due to loss of the stabilizing electronic interaction of the nitrogen π-donor with the (CO)$_5$Cr acceptor unit. Note that allenylidene pentacarbonyl complexes lacking a stabilizing interaction of the CR$_2$ group with the [(CO)$_5$M] fragment are rather unstable. As an example, [(CO)$_5$Cr=C=C=CMe$_2$] has not been isolated until now and [(CO)$_5$Cr=C=C=CPh$_2$] has been isolated but quickly decomposes in solution at room temperature.[13h]

Scheme 8



Spectroscopic Results. The ν(CO) vibrations and the ν(CCC) absorption in allenylidene carbonyl complexes are sensitive probes for the electronic interaction of the terminal substituents with the carbonyl metal fragment.[16,17h,k,18,19] All allenylidene complexes exhibit spectroscopic features characteristic for π-donor-substituted allenylidene complexes. The absorptions are found at rather low energy and are comparable to those of amino(alkoxy)allenylidene complexes,[16] indicating pronounced donor character of the ligand (see resonance forms **B′** and **B″** in Scheme 1). However, the comparison of the vibrations of **3a**, **4a**, **6a**−**17a**, and **20a** with those of unsubstituted **5a**[16] (Table 1) suggests that neither substitution of the pyridyl ring of the allenylidene ligand nor elongation of the conjugated chain (**11a** → **12a** → **13a**) strongly influences the electron distribution within the "(CO)$_5$M=C=C=C" fragment. In contrast, replacing one CO ligand by a phosphine considerably reduces the importance of the zwitterionic iminium−alkynyl resonance forms **B′** and **B″** relative to that of the cumulene form **A** (Scheme 1), as has already been observed.[20]

The chemical shifts of the allenylidene carbon atoms of the new complexes (Table 1) agree well with those of the known

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Table 1. Selected Spectroscopic Data for the Allenylidene Complexes 1a,b−6a,b and 7a−20a[a]

compd	ν(CO)	ν(CCC)[b]	$\delta(C_\alpha)$	$\delta(C_\beta)$	$\delta(C_\gamma)$	λ_{max}
1a	2076, 1933, 1907	2000	200.9	117.9	139.9	544
1b	2080, 1927,1900	2003	178.7	115.6	141.5	523
2a	2076, 1933, 1907	2000	201.5	117.8	138.9	543
2b	2080, 1927, 1900	2003	179.3	115.5	138.9	523
3a	2077, 1930, 1905	2005	190.5	113.2	139.7	512
3b	2080, 1925, 1899	2008	170.8	111.5	140.6	495
4a	2078, 1930, 1904	2005	191.1	111.5	136.0	511
4b	2081, 1924, 1898	2006	170.0	109.5	137.1	494
5a[16]	2076, 1929, 1901	2012	186.1	111.6	139.0	479
5b[16]	2079, 1922, 1894	2016	166.0	109.7	139.2	464
6a	2078, 1930, 1905	2002	193.7	113.4	136.4	513
6b	2081, 1925, 1898	2004	172.5	111.1	137.3	496
7a	2077, 1930, 1903	2003	190.3	112.1	135.7	502
8a	2078, 1931, 1904	2003	192.6	112.9	135.8	516
9a	2077, 1931, 1904	2001	192.9	113.1	135.9	522
10a	2078, 1931, 1904	2001	193.2	116.5	135.8	522
11a	2077, 1930, 1903	2002	190.1	112.4	137.7	519
12a	2077, 1931, 1904	2002	192.9	113.0	135.7	520
13a	2078, 1931, 1904	2001	185.0	113.1	135.9	522
14a	2077, 1930, 1902	2009	185.7	111.9	138.3	524
15a	2077, 1930, 1904	2003	193.2	115.8	136.3	514
16a	Cr−CO: 2078, 1928, 1899 Ru−CO: 2045, 1996	2009	182.7	110.6	134.3	487
17a	Cr−CO: 2077, 1928, 1899 Fe−CO: 2017, 1972	2009	181.6	110.6	133.7	492
18a	2077, 1933, 1906	1993	198.2	114.7	136.1	575
19a	2037, 1896, 1887, 1857	1968	206.4	118.4	137.8	539
20a	Cr−CO: 2076, 1930, 1904 Co−CO: 2095, 2060, 2033	2001	189.3	120.0	138.1	522

[a] IR absorptions in cm^{-1} in THF, ^{13}C NMR data in ppm in d_6-acetone, λ_{max} in nm in CH_2Cl_2. [b] Dominant character ν(CCC): however, there is considerable mixing of the ν(CCC) with ν(CO) A_1 vibrations.

pyridyl allenylidene complexes **5a,b**.[16] In comparison to the resonance of the C_α atom of nondonor-substituted allenylidene complexes,[21] that of **3a−20a** is found at significantly lower field. The substitution pattern of the pyridyl ring only slightly influences the ^{13}C allenylidene resonances, and this matches well with our observations from IR spectroscopy.

The UV/vis spectra of the complexes **3a**, **4a**, and **6a−17a** show an intense metal-to-ligand charge transfer (MLCT) absorption in the range 487 (**16a**)−524 nm (**14a**). The λ_{max} values of **3a**, **4a**, and **6a−15a** are nearly independent of the substitution pattern and of the elongation of the unsaturated chain, indicating significant interactions between the allenylidene chromophore and the substituents at the pyridyl ring. In comparison to the unsubstituted complex **5a**, all absorptions are shifted to lower energy. As expected, the phosphine-substituted complex **19a** absorbs at even lower energy, consistent with a rise in energy of the mostly metal-localized HOMO.

The molecular structures of **2a** and **19a** were additionally established by X-ray structural analyses (Figures 1 and 2). The structures exhibit all features usually observed with aminoallenylidene complexes.[16,17k,18,19,22] The C_α−C_β bond (C6−C7 in **2a** and C5−C6 in **19a**) is rather short and corresponds to an elongated C−C triple bond. Conversely, the C_β−C_γ bond (1.394(5) Å in **2a**, 1.397(5) Å in **19a**) is long, in accord with a significant contribution of the resonance form **B′** (Scheme 1). The M−C_3 fragment deviates slightly from linearity in both complexes. The plane of the allenylidene ligand in **2a** eclipses the cis-CO groups (torsion angle C(1)−Cr(1)−C(8)−N(1) = 34.2°). A comparison of the individual bond distances in **2a** with those in **5a** indicates that the annulated ring reduces the π-donor properties of the terminal substituent. The conclusion is also supported by the IR data.

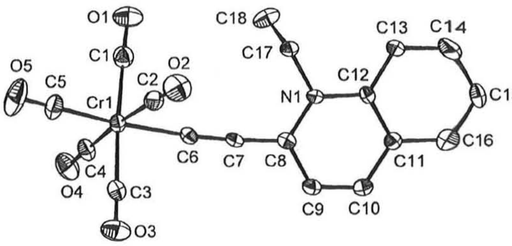

Figure 1. Plot of complex **2a** (ellipsoids drawn at the 50% probability level, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Cr(1)−C(1) = 1.905(4), Cr(1)−C(2) = 1.909(4), Cr(1)−C(3) = 1.901(4), Cr(1)−C(4) = 1.901(4), Cr(1)−C(5) = 1.886(4), Cr(1)−C(6) = 2.015(4), C(6)−C(7) = 1.239(5), C(7)−C(8) = 1.394(5), C(8)−N(1) = 1.370(4), C(8)−C(9) = 1.415(5); Cr(1)−C(6)−C(7) = 173.0(3), C(6)−C(7)−C(8) = 175.4(3).

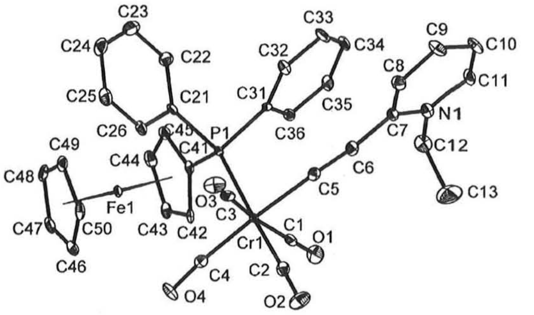

Figure 2. Plot of complex **19a** (ellipsoids drawn at the 50% probability level, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Cr(1)−P(1) = 2.395(1), Cr(1)−C(1) = 1.877(4), Cr(1)−C(2) = 1.861(4), Cr(1)−C(3) = 1.887(4), Cr(1)−C(4) = 1.856(3), Cr(1)−C(5) = 2.009(4), C(5)−C(6) = 1.234(5), C(6)−C(7) = 1.397(5), C(7)−N(1) = 1.373(4), C(7)−C(8) = 1.400(5); Cr(1)−C(5)−C(6) = 176.4(3), C(5)−C(6)−C(7) = 173.0(4).

In **19a** the P−Cr axis is nearly perpendicular to the allenylidene plane (torsion angle P(1)−Cr(1)−C(7)−N(1) = −78.3°), thus optimizing back-donation into the allenylidene ligand. As expected, both Cr−CO_{cis} distances (Cr(1)−C(1) and Cr(1)−C(3)) are shorter than the Cr−CO_{trans} bonds, Cr(1)−C(4) and Cr(1)−C(2) being very similar.

Electrochemistry and Spectroelectrochemistry of 11a−13a and 19a. The ferrocenyl unit in **11a−13a** bonded to the terminal carbon atom of the chain is readily oxidized. The cyclic voltammograms of **11a−13a** display in CH_2Cl_2/[NBu_4]PF_6 a fully reversible one-electron wave in the range +1.2/−1.0 V vs the saturated calomel electrode (SCE) (Table 2). This redox process corresponds to the well-known ferrocene-centered oxidation and, as expected, indicates that the Fe(III) forms are stable on the time scale of the voltammetric experiment.

It is immediately apparent that the carbon-rich alkynylallenylidene pentacarbonyl metal substituents are electron-withdrawing and make the oxidation of **11a−13a** more difficult than

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(22) (a) Fischer, E. O.; Kalder, H. J.; Frank, A.; Köhler, F. H.; Huttner, G. *Angew. Chem.* **1976**, *88*, 683; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 623. (b) Duetsch, M.; Stein, F.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Organometallics* **1993**, *12*, 2556. (c) Aumann, R. *Chem. Ber.* **1994**, *127*, 725.

Table 2. Electrochemical Data[a] for Complexes 11a–14a and 19a in CH_2Cl_2

compd	$E°_1$ (V)	ΔE (mV)	$E°_2$ (mV)	ΔE (mV)	i_{rev}/i_f
11a	614(5)	90			1
12a	582(5)	100			1
13a	593(5)	80			1
14a	605(5)	80	720(5)	66	1
19a	165(5)	70	750(5)	70	1

[a] Conditions: $E°$ versus a saturated calomel electrode (SCE), 0.1 M $(n\text{-}Bu)_4N^+[PF_6]^-$ at 25 °C.

that of ferrocene (0.460 V vs SCE).[23] The electron-withdrawing properties of the alkynylallenylidene pentacarbonyl metal moieties in **11a**–**13a** are smaller than those of the pentacarbonyl carbene chromium fragment in $[(CO)_5Cr{=}C(OEt)Fc]$ (0.77 V)[24] but more pronounced than those of the pentacarbonyl alkenylcarbene chromium fragment in $[(CO)_5Cr{=}C(OEt)(CH{=}CH)_nFc]$ ($n = 1$, 0.595 V; $n = 2$, 0,536 V; $n = 3$, 0.494 V).[25]

A comparison of the redox potentials of compounds **11a** and **12a** shows that the introduction of an ethynylbenzene spacer between the pyridyl-substituted allenylidene entity and the redox-active ferrocenyl group slightly diminishes the electron-withdrawing effect of the chromium carbonyl building block on the iron center. However, introduction of a second ethynylbenzene fragment (**12a** → **13a**) has only a negligible effect on the redox potential of the complex. It thus seems that the electron-withdrawing properties of the ethynylbenzene group compensate the electronic effects of the increasing separation of the push–pull groups.

In contrast to **11a**–**13a**, the cyclic voltammogram of **19a** displays two reversible one-electron waves (Table 2, Figure 3) and, in addition, an irreversible oxidation (at ca. 1.15 V) and reduction wave (not shown in Figure 3). The irreversible reduction is very likely due to reduction of the allenylidene unit. DFT calculations show that the LUMO of **19a** is predominantly localized within the allenylidene ligand. Studies on mono- and binuclear ruthenium allenylidene complexes[14b–i] also indicate that reduction is ligand-centered. The first reversible oxidation wave ($E° = 0.165$ V) is assigned to oxidation of essentially the chromium atom. At first glance, such an assignment seems rather unusual since (a) the first oxidation in **11a**–**13a** is ferrocene-centered and (b) the oxidation of pentacarbonyl carbene chromium complexes is usually observed at much higher potential.[26] However, the assignment is supported by several observations.

(a) From calculations on **19a** it follows that the HOMO is mostly localized on chromium.

(b) The corresponding ferrocene-free complex *cis*-$[(CO)_4(PPh_3)Cr{=}C{=}C{=}C\{-N(Et)(CH)_4-\}]$ likewise exhibits a one-electron oxidation wave at 0.200 V in addition to a semireversible wave at 1.07 V.

(c) The ESR spectra of **19a**$[PF_6]$ (obtained by oxidation of **19a** with ferrocenium hexafluorophosphate) in THF or CH_2Cl_2 run at 77 K display a rhombic signal with main g components at $g_1 = 1.988$, $g_2 = 2.037$, and $g_3 = 2.069$. The signal is in agreement with a chromium-centered radical rather than with a ferrocene-centered oxidation. In addition, the high-field feature is split into a 1:1 doublet by coupling with a ^{31}P nucleus ($A_1 = 20.0$ G).

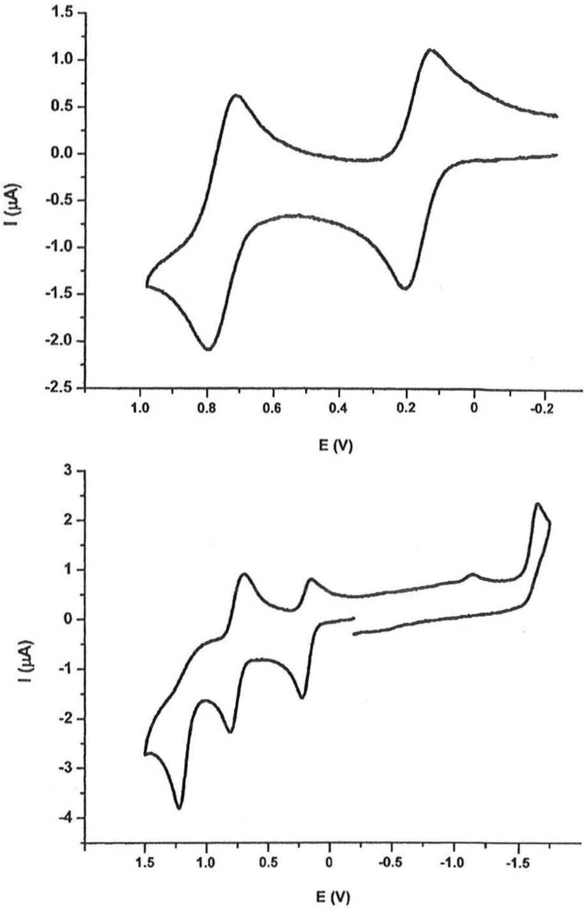

Figure 3. Cyclic voltammograms of **19a** at a Pt electrode in CH_2Cl_2 (0.1 M Bu_4NPF_6, 0.1 V s^{-1} at 20 °C; E versus SCE) in the range +0.95 to −0.25 V (above) and +1.5 to −1.75 V (below).

The first oxidation wave of **19a** is at a considerably less positive potential than that of $PFcPh_2$ ($E° = 0.565$ V),[27] of $[(CO)_5MPFcPh_2]$ (M = Mo, $E° = 0.735$ V; M = W, $E° = 0.760$ V),[27] and of $[(CO)_5Cr\text{-}PPh_2\{(C_5H_4)Fe(C_5H_4R)\}]$ (R = COOH, $E° = 0.735$ V;[28] R = C(=O)NMe$_2$, $E° = 0.79$ V[28]).

The second oxidation step observed for **19a** is tentatively assigned to oxidation of the ferrocene system. The assignment is supported by the similarity of the oxidation potential to that of the ferrocene-centered oxidation of **11a**–**13a** and by the results of DFT calculations on **19a**$^+$. These calculations indicate that the singly occupied highest orbital in **19a**$^+$ is localized on iron. However, and in contrast to these results, from the ESR spectra of **19a**$^+[PF_6]$ it follows that **19a**$^+$ is a chromium-centered radical (see above). Analogously to **19a**, two reversible oxidation waves were observed for the tetracarbonyl carbene phosphine chelate complex $[(CO)_4Cr{-}PPh_2\{(C_5H_4)Fe(C_5H_4CNMe_2)\}]$ ($E° = 0.33$ and 0.69 V).[29]

On the basis of the chemical reversibility of the redox process at the platinum electrode, the 17-electron Fe(III) complexes

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[**11a**−**13a**]$^+$X$^-$ were viewed as a possible viable synthetic target. However, oxidation of **11a** with AgOTf at −80 °C and precipitation of the salt [**11a**]$^+$OTf$^-$ by addition of cold pentane did not allow the isolation of a pure product but led to the decomposition of the compound. Therefore, we decided to check the stability of the monocation by ESR spectroscopy. A THF solution of **11a** was treated with 1 equiv of AgOTf at −80 °C and stirred for 10 min at this temperature before it was transferred into an ESR tube and frozen at liquid nitrogen temperature. An ESR spectrum run at 77 K displays a weakly anisotropic signal. Simulation of the experimental spectrum allowed the extraction of the tensor components for this axial pattern of $g_{\parallel} = 2.101$, $g_{\perp} = 2.069$, and $g_{\mathrm{iso}} = 2.079$. No proton hyperfine coupling was resolved. After the first spectrum was recorded, the ESR tube was placed in a bath at −20 °C for 30 min. Then another spectrum was run at 77 K under the same conditions. The intensity of the signal was not perturbed by the storage of the solution at −20 °C, indicating that the ESR-active species is stable in solution at this temperature.

It is well-known that for d^5 metallocenes the electronic ground state is very sensitive to the combination of the metal and the ligand orbitals.[30] In the case of ferrocenium the degenerate electronic configuration leads to a fast electronic relaxation; thus, ESR spectra can only be observed at very low temperature (∼4 K) and the signal shows an axial pattern with a large anisotropy ($g_{\parallel} > 4$ and $g_{\perp} < 1.5$).[31] The presence of the highly polarized and extended π-system linked to one of the C_5 rings of the ferrocenium produces a dramatic change in the ESR spectrum. The observation of a well-resolved signal at 77 K indicates that the radical [**11a**]$^+$ has a nondegenerate ground state. The weak anisotropy of the signal and the g_{iso} value close to the free-electron g value suggest that the carbon-rich fragment which connects the two metal centers significantly contributes to the delocalization of the spin density. The low chemical stability of the radical cation is a probable consequence of its particular electronic structure. Note that the decomposition of pentacarbonyl complexes of chromium, molybdenum, and tungsten is usually initiated by M−CO dissociation.

The first oxidation process of the complexes **11a**, **12a**, **14a**, and **19a** was additionally monitored by in situ IR and UV/vis spectroscopy. A succession of spectra was recorded, either while the potential was held at the appropriate value or while the respective voltammetric wave was very slowly scanned. The oxidation/re-reduction cycle was accompanied by some decomposition, due to the relative instability of the radical complexes. The spectroscopic yields of the respective starting complex after one complete oxidation/re-reduction cycle varied between 42 and 82% (**11a**, 42%; **12a**, 51%; **14a**, 69%; **19a**, 82%). With all compounds, oxidation of the allenylidene complexes causes a dramatic shift of the ν(CCC) and ν(CO) absorptions in the IR spectra. IR band positions of the neutral and oxidized species are given in Table 3. As representative examples spectra accumulated during gradual oxidation (Figures 4a and 5a) and re-reduction (Figures 4b and 5b) of complexes **12a** and **19a** are depicted in Figures 4 and 5.

Table 3. IR Spectroscopic Data of the Neutral Complexes 11a, 12a, 14a, and 19a and Their Monocations in 1,2-Dichloroethane

compd	ν(CO)			ν(CCC)^a	ν(C_γN)
11a	2077	1928	1903	2004	1515
11a$^+$	2113	2068	2028	1978	1518
12a	2080	1930	1901	2002	1518
12a$^+$	2123	2075	2029	1970	1520
14a	2080	1928	1900	2010	1549
14a$^+$	2122	2070	2031	1971	1560
19a	2039	1895	1884	1851	1969
19a$^+$	2076	2011	1989	1958	2031

^{a} There is considerable mixing of ν(CCC) with ν(CO) vibrations.

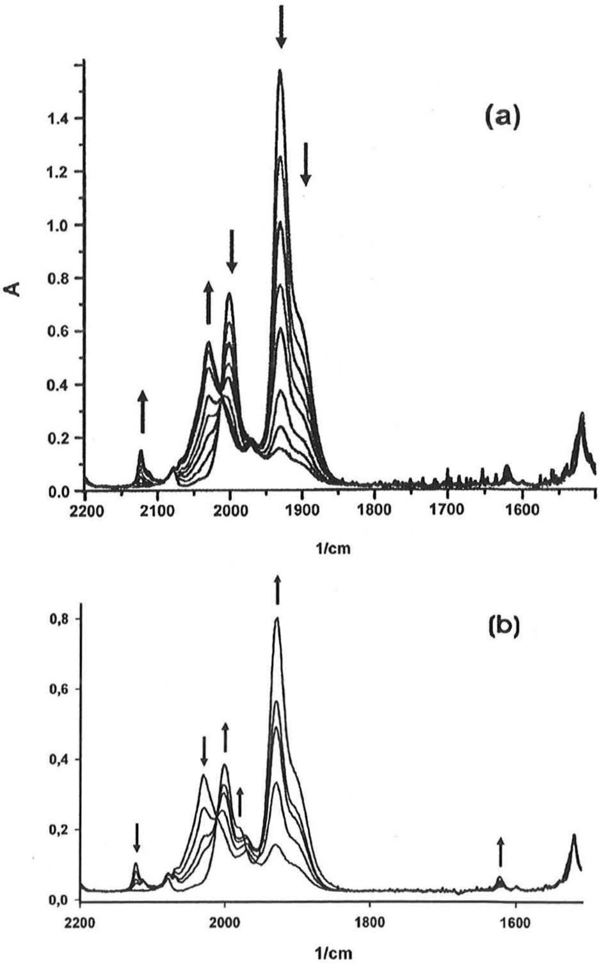

Figure 4. IR spectroelectrochemistry of complex **12a** in CH_2Cl_2: spectral changes accompanying oxidation (a) and re-reduction (b).

Upon iron-centered oxidation (see above) the absorptions of the pentacarbonyl chromium moiety shift toward higher energy. This hypsochromic shift is readily explained by a decrease in back-donation from chromium to the carbonyl ligands as a consequence of the reduced electron density at the metal. The shift is unusually large (up to 100 cm^{-1}) and implies considerable charge delocalization from iron to chromium and strong electronic interaction of the ferrocenyl and the $Cr(CO)_5$ moieties in [**11a**]$^+$, [**12a**]$^+$, and [**14a**]$^+$. These shifts are of the same order of magnitude as those observed upon oxidation of [$(C_6H_6)Cr(CO)_3$], where the redox-active ligand is directly bonded to chromium,[32] and significantly exceed those observed upon oxidation of the binuclear acetylenedithiolate-bridged complex

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[30] (a) Smart, J. C.; Robbins, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3936. (b) O'Hare, D.; Green, J. C.; Chadwick, T. P.; Miller, J. R. *Organometallics* **1988**, *7*, 1335.

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[32] Camire, N.; Nafady, A.; Geiger, W. E. *J. Am. Chem. Soc.* **2002**, *124*, 7260.

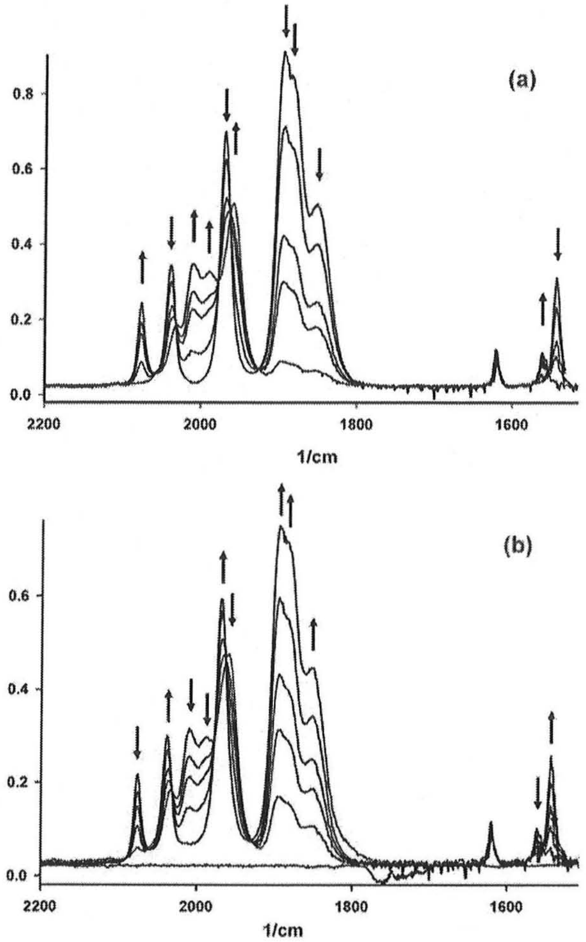

Figure 5. IR spectroelectrochemistry of complex **19a** in CH_2Cl_2: spectral changes accompanying oxidation (a) and re-reduction (b).

[Tp′(CO)$_2$W(C_2S_2)Ru(PPh_3)Cp].[33] In contrast, the ν(CCC) vibration in the oxidized species [**11a**]$^+$, [**12a**]$^+$, and [**14a**]$^+$ occurs at lower energy than in the corresponding neutral compounds. However, the effect of oxidation on the ν(CCC) vibration is less pronounced than that on the ν(CO) absorptions.

The influence of oxidation of the tetracarbonyl complex **19a** on the IR absorptions is comparable to that observed for **11a**, **12a**, and **14a**, thus confirming once more the strong interaction of the ferrocenyl with the pentacarbonyl chromium moieties in [**11a**]$^+$, [**12a**]$^+$, and [**14a**]$^+$. As expected, on oxidation the ν(CCC) vibration in **19a** shifts toward higher energy, due to reduced back-donation from chromium to the allenylidene ligand and thus increased importance of the alkynyl resonance forms **B′** and **B″** (Scheme 1). The enhanced contribution of these resonance forms also shows up in the shift of the ν(C−N) vibration of **19a** to higher wavenumbers (1543 cm^{-1} → 1561 cm^{-1}). This effect is most pronounced for complex **19a**, where the redox-active center is predominantly the chromium atom.

On oxidation, the MLCT absorption in the UV/vis spectra of **11a**, **12a**, **14a**, and **19a** shifts toward higher energy by 4600−6100 cm^{-1} (Table 4). The spectral changes accompanying the oxidation and re-reduction of complex **12a** are shown in Figure 6. The extent of the shift only slightly decreases on elongation of the chain (**11a** → **12a**) and increases when the ferrocenylethynyl substituent is moved from the 5-position ("para" to the CrC_2 fragment) into the 6-position ("meta" to CrC_2) (**11a** → **14a**). The large shifts observed again confirm the delocalization of the positive charge onto $Cr(CO)_5$, thus considerably reducing the propensity of the chromium−ligand fragment for back-donation. As expected, the influence of one-electron oxidation is most pronounced with **19a**. One should note again that the first oxidation of **19a** is assigned to (predominantly) the chromium center.

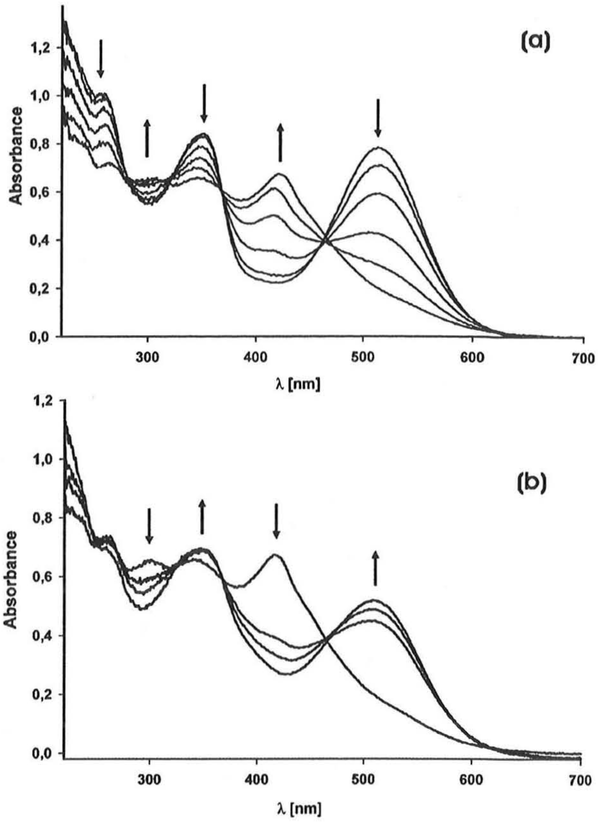

Figure 6. UV−vis spectroelectrochemistry of complex **12a** in CH_2Cl_2: spectral changes accompanying oxidation (a) and re-reduction (b).

Table 4. UV/Vis Spectroscopic Data of the Neutral Complexes 11a, 12a, 14a, and 19a (1*x*a), Their Monocations [1*x*a]$^+$, and Energy Difference of the Peak Maxima

	1*x*a			
	11a	**12a**	**14a**	**19a**
λ_{max} (nm)				
1*x*a	514	515	521	530
[**1*x*a**]$^+$	411	417	408	400
Δ (cm^{-1})	4900	4600	5300	6100

NLO Properties of Complexes 11a−13a. The cumulenylidene complexes **11a**−**13a** are polar push−pull systems and are expected to exhibit nonlinear optical properties.[34] Therefore, the complexes were subjected to hyper-Rayleigh scattering (HRS)[35] studies, but as they absorb substantially in the area of 532 nm (i.e., $I(2\omega)$ when the incident light has a wavelength of $I(\omega)$ = 1064 nm), the stimulating laser light was shifted to 1500 nm. The experiments were carried out in CH_2Cl_2 as described

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Table 5. Quadratic Hyperpolarizabilities for Complexes 11a−13a, $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)_2]$, and $[(CO)_5Cr{=}C{=}C{=}C{=}C{=}C(NMe_2)_2]$

complex	β (10^{-30} esu)[a]	β_0 (10^{-30} esu)[a]
11a[b]	0	0
12a[b]	20	9
$[(CO)_5Cr{=}C{=}C{=}C(NMe_2)_2]$[c]	21	9.5
13a[b]	73	33
$[(CO)_5Cr{=}C{=}C{=}C{=}C{=}C(NMe_2)_2]$[c]	100	31

[a] All values ±10%. [b] Conditions: in CH_2Cl_2, incident light 1500 nm. [c] Conditions: in DMF, incident light 1064 nm.

earlier.[36] As a reference Disperse Red 1 (DR 1; $\beta(CH_2Cl_2) = 70 \times 10^{-30}$ esu) was used.

The first hyperpolarizability β could only be obtained for the complexes **12a** and **13a** (Table 5). Surprisingly, complex **11a** did not show any intensity in the HRS experiment. In contrast, related donor-substituted allenylidene complexes exhibit moderate first hyperpolarizabilities. The β values of complex **12a** ($\beta = 20 \times 10^{-30}$ esu; $\beta_0 = 9 \times 10^{-30}$ esu) are comparable to those of $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)_2]$ ($\beta = 21 \times 10^{-30}$ esu; $\beta_0 = 9.5 \times 10^{-30}$ esu, in DMF).[34] Introduction of a second ethynylbenzene spacer between ferrocene and the heterocycle (**12a** → **13a**) almost quadruples β and β_0 (**13a**: $\beta = 73 \times 10^{-30}$ esu; $\beta_0 = 33 \times 10^{-30}$ esu). These values are close to those of the pentatetraenylidene complex $[(CO)_5Cr{=}C{=}C{=}C{=}C{=}C(NMe_2)_2]$ ($\beta = 100 \times 10^{-30}$ esu; $\beta_0 = 31 \times 10^{-30}$ esu, in DMF).[34] These results indicate that the extension of the π-system that is conjugated to the allenylidene chain seems to be less efficient than extension of the cumulenylidene carbon chain. The effect of extension of the π-system by a "$C{\equiv}CC_6H_4{-}$" unit (length ca. 6.9 Å) is on the same order of magnitude as that exerted by insertion of a "$C{=}C{=}$" unit (length ca. 2.6 Å) into the cumulenylidene chain.

Concluding Remarks

Pyridyl- and quinolinylallenylidene complexes are readily synthesized from pentacarbonyl tetrahydrofuran complexes by reaction with appropriate lithium alkynyl compounds followed by alkylation of the resulting alkynylmetalate. Palladium/copper-catalyzed coupling of bromo-functionalized pyridylallenylidene complexes offers access to a broad range of complexes with alkynyl functionalities in conjugation with the allenylidene carbon chain. Among others, organometallic end groups can easily be introduced, affording homo- as well as heterobinuclear complexes. All spectroscopic data of the new complexes agree well with those of comparable amino-substituted allenylidene complexes. These complexes are dipolar and are stable at room temperature, delocalization of the lone pair at nitrogen toward the pentacarbonylmetal fragment being a major stabilizing factor.

IR and UV/vis spectroscopic data reveal that in cationic binuclear complexes, obtained upon iron-centered one-electron oxidation of the ferrocenyl-terminated complexes, the positive charge is strongly delocalized, increasing the acceptor properties of the chromium pentacarbonyl moiety. The effect of the charge transfer on Cr−CO back-bonding is unusually large, demonstrating that such bridging alkynyl−allenylidene ligands efficiently mediate electronic communication between the terminal metal centers.

The first hypolarizability β of the allenylidene complexes with the most extended π-systems as measured by hyper-Rayleigh scattering methods are in the region of cumulenylidene complexes with comparable chain lengths. The effect of the electrochemical manipulation on the NLO properties is currently under investigation.

Experimental Section

All operations were performed under an inert gas atmosphere (nitrogen or argon) using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), $LiAlH_4$ (pentane), and sodium (THF, Et_2O). The silica gel used for chromatography (Baker, silica for flash chromatography) was argon-saturated and used without modifications. The reported yields refer to analytically pure compounds and are not optimized. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded with Jeol JNX 400, Varian Inova 400, and Bruker AC 250 spectrometers at ambient temperature. Chemical shifts are relative to the residual solvent or tetramethylsilane peaks (^1H, ^{13}C) or 100% H_3PO_4 (^{31}P). IR spectra were recorded on a Biorad FTS 60 or a Perkin-Elmer Paragon 1000Pc. UV/vis spectra were recorded on either a Hewlett-Packard 8453 diode array spectrophotometer or a Bruins Instruments Omega 10 spectrophotometer. MS measurements were carried out on a Finnigan MAT 312 instrument. Elemental analyses were carried out on a Heraeus CHN-O-Rapid instrument. X-band ESR spectra were recorded on a Bruker EMX-8/2.7 spectrometer, and simulated spectra were obtained with the Bruker SIMFONIA program. The following compounds were synthesized according to literature procedures: 2-ethynylquinoline,[37] 5-bromo-2-ethynylpyridine,[38] 6-bromo-2-ethynylpyridine,[39] diphenylferrocenylphosphane,[40] 4-ethynyltolane,[41] ethynylferrocene,[42] 1-ethynyl-4-(ferrocenylethynyl)benzene,[43] 1-(ferrocenylethynyl)-4-(phenylethynyl)benzene,[43] 1,4-bis(ethynyl)benzene,[44] bromodicarbonyl(η^5-cyclopentadienyl)ruthenium,[45] and bromodicarbonyl(η^5-pentamethylcyclopentadienyl)iron.[45] All other chemicals were used as received from commercial suppliers.

Preparation of the Complexes 1−4. A solution of 3.1 mL of *n*BuLi (5 mmol, 1.6 M in hexane) was added dropwise at −80 °C (**1**, **2**) or at −100 °C (**3**, **4**) to a solution of 5 mmol of the appropriate alkyne (2-ethynylquinoline for **1** and **2**; 5-bromo-2-ethynylpyridine for **4**; 6-bromo-2-ethynylpyridine for **3**) in 50 mL of dry THF. The solution was stirred for 20 min at this temperature. Then 50 mL of a solution of $[(CO)_5M(THF)]$ (M = Cr, W; 0.1 M in THF) was added. The cooling bath was removed, and the brown solution was warmed to ambient temperature. After stirring for 30 min, the solvent was removed in vacuo. The remaining oily residue was dissolved in 50 mL of dry CH_2Cl_2 and treated with 5 mmol of $R_3O[BF_4]$ (R = Me, Et) at 0 °C and this mixture was stirred for a further 60 min at 0 °C. The resulting solution was filtered at −20 °C through a 5 cm layer of silica using CH_2Cl_2 as the eluent. The solvent was evaporated and the residue chromatographed at −20 °C on silica using mixtures of pentane and CH_2Cl_2 as the eluent. First, with pentane/CH_2Cl_2 (2/1) a pale yellow band containing $[M(CO)_6]$ (M = Cr, W) was obtained. Then, with pentane/CH_2Cl_2 (polarity increasing from 1/1 to 1/3) a strongly colored band

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containing the product complexes **1**−**4** was eluted. In the synthesis of **3** and **4** the pyridinylallenylidene complexes **5a**[16] and **5b**[16] (pentane/CH_2Cl_2 1/4) were isolated as side products in low yield (<5%).

Pentacarbonyl(*N*-methyl-3-hydroquinoline-1,2-propadienylidene)chromium (1a). Yield: 1.33 g (74%), deep violet solid. Mp: 125−128 °C. IR (THF): ν(CO, CCC) 2076 vw, 2000 m, 1933 vs, 1907 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 3.59 (s, 3H, NCH_3), 7.59 (d, $^3J_{HH}$ = 9.0 Hz, 1H, Quin H), 7.76 (t, $^3J_{HH}$ = 8.2 Hz, 1H, Quin H), 8.05 (t, $^3J_{HH}$ = 8.2 Hz, 1H, Quin H), 8.13 (m, 2H, Quin H), 8.52 (d, $^3J_{HH}$ = 9.0 Hz, 1H, Quin H). ^{13}C NMR (100 MHz, d_6-acetone): δ 40.2 (NCH_3), 117.9 (C_β), 118.6, 126.7, 127.3, 128.0, 130.6, 134.8, 140.1, 141.9 (8 Quin C), 139.9 (C_γ), 200.9 (C_α), 219.2 (cis-CO), 224.0 (trans-CO). EI (MS): *m*/*z* (%) 359 (41) [M$^+$], 275 (16) [(M − 3CO)$^+$], 247 (50) [(M − 4CO)$^+$], 219 (100) [(M − 5CO)$^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 544 (4.361). Anal. Calcd for $C_{17}H_9CrNO_5$ (359.56): C, 56.84; H, 2.53; N, 3.90. Found: C, 57.07; H, 2.72; N, 3.96.

Pentacarbonyl(*N*-methyl-3-hydroquinoline-1,2-propadienylidene)tungsten (1b). Yield: 1.75 g (71%), deep violet solid. Mp: 101−104 °C. IR (THF): ν(CO, CCC) 2080 vw, 2003 m, 1927 vs, 1900 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 4.62 (s, 3H, NCH_3), 7.66 (d, $^3J_{HH}$ = 8.6 Hz, 1H, Quin H), 7.78 (td, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, Quin H), 8.09 (td, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Quin H), 8.17 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, Quin H), 8.24 (d, $^3J_{HH}$ = 7.6 Hz, 1H, Quin H), 8.61 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Quin H). ^{13}C NMR (100 MHz, d_6-acetone): δ 40.6 (NCH_3), 115.6 (C_β), 118.8, 126.9, 127.5, 128.3, 130.7, 134.9, 140.1, 142.4 (8 Quin C), 141.5 (C_γ), 178.7 (C_α), 198.4 (cis-CO, $^1J_{WC}$ = 121.2 Hz), 203.3 (trans-CO). EI (MS): *m*/*z* (%) 491 (8) [M$^+$], 463 (10) [(M − CO)$^+$], 435 (11) [(M − 2CO)$^+$], 351 (44) [(M − 5CO)$^+$], 268 (100) [W(CO)$_4^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 523 (4.413). Anal. Calcd for $C_{17}H_9NO_5W$ (491.11): C, 41.58; H, 1.85; N, 2.85. Found: C, 41.68; H, 1.78; N, 2.91.

Pentacarbonyl(*N*-ethyl-3-hydroquinoline-1,2-propadienylidene)chromium (2a). Yield 1.26 g (68%), deep violet solid. Mp: 108−110 °C. IR (THF): ν(CO, CCC) 2076 vw, 2000 m, 1933 vs, 1907 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 1.60 (t, $^3J_{HH}$ = 7.0 Hz, 3H, NCH_2CH_3), 5.13 (q, $^3J_{HH}$ = 7.0 Hz, 3H, NCH_2CH_3), 7.53 (d, $^3J_{HH}$ = 9.1 Hz, 1H, Quin H), 7.72 (t, $^3J_{HH}$ = 8.0 Hz, 1H, Quin H), 8.03 (t, $^3J_{HH}$ = 8.0 Hz, 1H, Quin H), 8.13 (m, 2H, Quin H), 8.48 (d, $^3J_{HH}$ = 9.1 Hz, 1H, Quin H). ^{13}C NMR (100 MHz, d_6-acetone): δ 13.4 (NCH_2CH_3), 48.5 (NCH_2CH_3), 117.8 (C_β), 118.1, 127.0, 127.9, 128.0, 130.9, 134.9, 140.3, 142.2 (8 Quin C), 138.9 (C_γ), 201.5 (C_α), 219.1 (cis-CO), 224.1 (trans-CO). EI (MS): *m*/*z* (%) 373 (32) [M$^+$], 289 (17) [(M − 3CO)$^+$], 261 (41) [(M − 4CO)$^+$], 233 (100) [(M − 5CO)$^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 543 (4.385). Anal. Calcd for $C_{18}H_{11}CrNO_5$ (373.29): C, 57.92; H, 2.97; N, 3.75. Found: C, 58.00; H, 3.09; N, 3.94.

Pentacarbonyl(*N*-ethyl-3-hydroquinoline-1,2-propadienylidene)tungsten (2b). Yield: 2.02 g (80%), deep violet solid. Mp: 93−95 °C. IR (THF): ν(CO, CCC) 2080 vw, 2003 m, 1927 vs, 1900 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 1.50 (t, $^3J_{HH}$ = 7.4 Hz, 3H, NCH_2CH_3), 5.02 (q, $^3J_{HH}$ = 7.4 Hz, 2H, NCH_2CH_3), 7.46 (d, $^3J_{HH}$ = 7.6 Hz, 1H, Quin H), 7.59 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Quin H), 7.91 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Quin H), 8.00 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Quin H), 8.10 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Quin H), 8.44 (d, $^3J_{HH}$ = 7.2 Hz, 1H, Quin H). ^{13}C NMR (100 MHz, d_6-acetone): δ 13.4 (NCH_2CH_3), 48.7 (NCH_2CH_3), 115.5 (C_β), 118.2, 127.2, 127.3, 128.1, 130.9, 134.9, 140.1, 142.4 (8 QuinC), 138.9 (C_γ), 179.3 (C_α), 198.3 (cis-CO, $^1J_{WC}$ = 125.0 Hz), 203.3 (trans-CO, $^1J_{WC}$ = 132.8 Hz). EI (MS): *m*/*z* (%) 505 (28) [M$^+$], 477 (17) [(M − CO)$^+$], 449 (51) [(M − 2CO)$^+$], 421 (33) [(M − 3CO)$^+$], 391 (31) [(M − 4CO)$^+$], 363 (63) [(M − 5CO)$^+$], 268 (100) [W(CO)$_4^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 523 (4.431). Anal. Calcd for $C_{18}H_{11}NO_5W$ (505.14): C, 42.80; H, 2.19; N, 2.77. Found: C, 43.03; H, 2.26; N, 2.78.

Pentacarbonyl(5-bromo-*N*-ethyl-3-hydropyridine-1,2-propadienylidene)chromium (3a). Yield: 0.90 g (45%), red solid. Mp: 112−114 °C. IR (THF): ν(CO, CCC) 2077 vw, 2005 m, 1930 vs, 1905 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 1.50 (t, $^3J_{HH}$ = 7.4 Hz, 3H, NCH_2CH_3), 4.31 (q, $^3J_{HH}$ = 7.0 Hz, 2H, NCH_2CH_3), 7.49 (dd, $^3J_{HH}$ = 8.2 Hz, $^2J_{HH}$ = 1.2 Hz, 1H, Pyr H), 7.70 (dd, $^3J_{HH}$ = 7.8 Hz, $^2J_{HH}$ = 1.2 Hz, 1H, Pyr H), 7.86 (t, $^3J_{HH}$ = 8.2 Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 13.1 (NCH_2CH_3), 56.0 (NCH_2CH_3), 113.2 (C_β), 127.4, 130.1, 134.3, 143.4 (4 Pyr C), 139.7 (C_γ), 190.5 (C_α), 219.3 (cis-CO), 223.7 (trans-CO). FAB (MS): *m*/*z* (%) 401 (21) [M$^+$], 373 (19) [(M − CO)$^+$], 345 (27) [(M − 2CO)$^+$], 317 (22) [(M − 3CO)$^+$], 289 (100) [(M − 4CO)$^+$], 261 (70) [(M − 5CO)$^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 512 (4.289). Anal. Calcd for $C_{14}H_8BrCrNO_5$ (402.12): C, 41.82; H, 2.01; N, 3.48. Found: C, 41.97; H, 2.12; N, 3.50.

Pentacarbonyl(5-bromo-*N*-ethyl-3-hydropyridine-1,2-propadienylidene)tungsten (3b). Yield: 0.91 g (34%), red solid. Mp: 93−95 °C. IR (THF): ν(CO, CCC) 2080 vw, 2008 m, 1925 vs, 1899 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 1.61 (t, $^3J_{HH}$ = 7.0 Hz, 3H, NCH_2CH_3), 5.05 (q, $^3J_{HH}$ = 7.1 Hz, 2H, NCH_2CH_3), 7.62 (dd, $^3J_{HH}$ = 8.2 Hz, $^2J_{HH}$ = 1.2 Hz, 1H, Pyr H), 7.83 (dd, $^3J_{HH}$ = 7.8 Hz, $^2J_{HH}$ = 1.2 Hz, 1H, Pyr H), 7.98 (t, $^3J_{HH}$ = 8.1 Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 13.2 (NCH_2CH_3), 56.2 (NCH_2CH_3), 111.5 (C_β, $^2J_{WC}$ = 25.0 Hz), 127.9, 130.3, 134.7, 143.5 (4 Pyr C), 140.6 (C_γ), 170.8 (C_α, $^1J_{WC}$ = 100.0 Hz), 198.4 (cis-CO, $^1J_{WC}$ = 125.0 Hz), 203.0 (trans-CO, $^1J_{WC}$ = 131.7 Hz). FAB (MS): *m*/*z* (%) 535 (80) [M$^+$], 507 (100) [(M − CO)$^+$], 479 (92) [(M − 2CO)$^+$], 451 (21) [(M − 3CO)$^+$], 395 (31) [(M − 5CO)$^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 495 (4.326). Anal. Calcd for $C_{14}H_8BrNO_5W$ (533.98): C, 31.49; H, 1.51; N, 2.62. Found: C, 31.58; H, 1.50; N, 2.74.

Pentacarbonyl(6-bromo-*N*-ethyl-3-hydropyridine-1,2-propadienylidene)chromium (4a). Yield: 0.94 g (47%), red solid. Mp: 123 °C dec. IR (THF): ν(CO, CCC) 2078 vw, 2005 m, 2010 m, 1930 vs, 1904 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 1.53 (t, $^3J_{HH}$ = 7.2 Hz, 3H, NCH_2CH_3), 4.64 (q, $^3J_{HH}$ = 7.2 Hz, 2H, NCH_2CH_3), 7.42 (d, $^3J_{HH}$ = 8.9 Hz, 1H, Pyr H), 8.15 (dd, $^3J_{HH}$ = 8.8 Hz, $^2J_{HH}$ = 2.2 Hz, 1H, Pyr H), 8.73 (d, $^2J_{HH}$ = 2.2 Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 14.7 (NCH_2CH_3), 55.3 (NCH_2CH_3), 111.5 (C_β), 113.9, 131.3, 144.1, 145.3 (4 Pyr C), 136.0 (C_γ), 191.1 (C_α), 219.2 (cis-CO), 223.5 (trans-CO). FAB (MS): *m*/*z* (%) 402 (31) [M$^+$], 373 (5) [(M − CO)$^+$], 345 (26) [(M − 2CO)$^+$], 317 (27) [(M − 3CO)$^+$], 289 (41) [(M − 4CO)$^+$], 261 (100) [(M − 5CO)$^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 511 (4.235). Anal. Calcd for $C_{14}H_8BrCrNO_5$ (402.12): C, 41.82; H, 2.01; N, 3.48. Found: C, 41.79; H, 2.07; N, 3.55.

Pentacarbonyl(6-bromo-*N*-ethyl-3-hydropyridine-1,2-propadienylidene)tungsten (4b). Yield: 0.53 g (20%), red solid. Mp: 101−103 °C. IR (THF): ν(CO, CCC) 2081 vw, 2014 m, 2006 m, 1924 vs, 1898 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 1.53 (t, $^3J_{HH}$ = 7.2 Hz, 3H, NCH_2CH_3), 4.64 (q, $^3J_{HH}$ = 7.2 Hz, 2H, NCH_2CH_3), 7.47 (d, $^3J_{HH}$ = 8.6 Hz, 1H, Pyr H), 8.22 (dd, $^3J_{HH}$ = 9.0 Hz, $^2J_{HH}$ = 2.3 Hz, 1H, Pyr H), 8.81 (d, $^2J_{HH}$ = 2.0 Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 14.8 (NCH_2CH_3), 55.6 (NCH_2CH_3), 109.5 (C_β), 114.6, 131.6, 144.5, 145.6 (4 Pyr C), 137.1 (C_γ), 170.0 (C_α), 198.4 (cis-CO, $^1J_{WC}$ = 125.0 Hz), 202.8 (trans-CO, $^1J_{WC}$ = 130.1 Hz). FAB (MS): *m*/*z* (%) 535 (80) [M$^+$], 507 (44) [(M − CO)$^+$], 479 (80) [(M − 2CO)$^+$], 451 (87) [(M − 3CO)$^+$], 395 (100) [(M − 5CO)$^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 494 (4.324). Anal. Calcd for $C_{14}H_8BrNO_5W$ (533.98): C, 31.49; H, 1.51; N, 2.62. Found: C, 31.70; H, 1.55; N, 2.81.

General Procedure for the Coupling of Complexes 3 and 4 with Terminal Alkynes. A solution of 1 mmol of the complexes **3**/**4**, 1 mL of triethylamine, and 5 equiv of the appropriate terminal alkyne in 5 mL of dry THF was degassed in three freeze−pump cycles. Then 0.35 g (5 mol %) of [$(PPh_3)_2PdCl_2$] and 0.02 g (10 mol %) of CuI were added. The solution was stirred until all of the starting material was consumed (as indicated by TLC). The solvent was evaporated and the residue chromatographed on silica at −20 °C using mixtures of pentane and CH_2Cl_2 as the eluent.

Pentacarbonyl{*N*-ethyl-6-[(trimethylsilyl)ethynyl]-3-hydropyridine-1,2-propadienylidene}chromium (6a). Yield: 0.42 g (99%), red solid. Mp: 89 °C. IR (THF): ν(CO, CCC) 2078 vw, 2002 m, 1930 vs, 1905 m cm^{-1}. ^1H NMR (400 MHz, d_6-acetone): δ 0.24 (s, 3H, $Si(CH_3)_3$), 1.63 (t, $^3J_{HH} = 7.0$ Hz, 3H, NCH_2CH_3), 4.75 (q, $^3J_{HH} = 7.1$ Hz, 2H, NCH_2CH_3), 7.54 (d, $^3J_{HH} = 8.6$ Hz, 1H, Pyr H), 8.07 (dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 1.6$ Hz, 1H, Pyr H), 8.75 (d, $^4J_{HH} = 1.6$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 0.1 ($Si(CH_3)_3$), 15.3 (NCH_2CH_3), 55.8 (NCH_2CH_3), 99.4 ($C\equiv C$), 102.5 ($C\equiv C$), 113.4 (C_β), 116.9, 131.0, 144.7, 146.9 (4 Pyr C), 136.4 (C_γ), 193.7 (C_α), 219.7 (cis-CO), 224.2 (trans-CO). FAB (MS): *m/z* (%) 419 (9) [M^+], 363 (10) [$(M - 2CO)^+$], 335 (11) [$(M - 3CO)^+$], 307 (67) [$(M - 4CO)^+$], 279 (100) [$(M - 5CO)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 513 (4.314). Anal. Calcd for $C_{19}H_{17}NO_5SiCr$ (419.43): C, 54.41; H, 4.09; N, 3.34. Found: C, 53.91; H, 4.02; N, 3.01.

Pentacarbonyl{*N*-ethyl-6-[(trimethylsilyl)ethynyl]-3-hydropyridine-1,2-propadienylidene}tungsten (6b). Yield: 0.25 g (46%), red solid. Mp: 81−82 °C. IR (THF): ν(CO, CCC) 2081 vw, 2004 m, 1925 vs, 1898 m cm^{-1}. ^1H NMR (400 MHz, d_6-acetone): δ 0.24 (s, 3H, $Si(CH_3)_3$), 1.64 (t, $^3J_{HH} = 7.0$ Hz, 3H, NCH_2CH_3), 4.75 (q, $^3J_{HH} = 7.1$ Hz, 2H, NCH_2CH_3), 7.59 (d, $^3J_{HH} = 8.4$ Hz, 1H, Pyr H), 8.12 (dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 2.3$ Hz, 1H, Pyr H), 8.81 (d, $^4J_{HH} = 2.2$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ −0.28 ($Si(CH_3)_3$), 15.0 (NCH_2CH_3), 55.7 (NCH_2CH_3), 99.1 ($C\equiv C$), 102.6 ($C\equiv C$), 111.1 (C_β), 117.2, 131.0, 144.6, 147.0 (4 Pyr C), 137.3 (C_γ), 172.5 (C_α), 198.6 (cis-CO, $^1J_{WC} = 123.0$ Hz), 203.2 (trans-CO, $^1J_{WC} = 132.6$ Hz). FAB (MS): *m/z* (%) 551 (90) [M^+], 523 (100) [$(M - CO)^+$], 495 (82) [$(M - 2CO)^+$], 411 (17) [$(M - 5CO)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 496 (4.350). Anal. Calcd for $C_{19}H_{17}NO_5SiW$ (551.28): C, 41.40; H, 3.11; N, 2.54. Found: C, 42.98; H, 3.34; N, 2.10.

Pentacarbonyl[*N*-ethyl-6-(*n*-dodec-1-ynyl)-3-hydropyridine-1,2-propadienylidene]chromium (7a). Yield: 0.33 g (67%), red oil. IR (THF): ν(CO, CCC) 2077 vw, 2003 m, 1930 vs, 1903 m cm^{-1}. ^1H NMR (400 MHz, d_6-acetone): δ 0.74 (t, $^3J_{HH} = 7.0$ Hz, 3H, $C_{10}H_{21}$), 1.17 (m, 12H, $C_{10}H_{21}$), 1.32 (m, 2H, $C_{10}H_{21}$), 1.46 (m, 2H, $C_{10}H_{21}$), 1.50 (t, $^3J_{HH} = 7.4$ Hz, 3H, NCH_2CH_3), 2.37 (t, $^3J_{HH} = 7.0$ Hz, 3H, CH_2CH_3), 4.62 (q, $^3J_{HH} = 7.4$ Hz, 2H, NCH_2CH_3), 7.41 (d, $^3J_{HH} = 8.5$ Hz, 1H, Pyr H), 7.91 (dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 1.9$ Hz, 1H, Pyr H), 8.54 (d, $^4J_{HH} = 2.1$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 14.3 ($C_{10}H_{21}$), 14.9 (NCH_2CH_3), 19.7, 23.3, 29.0, 29.5, 29.8, 30.0, 30.2, 32.6 ($C_{10}H_{21}$), 55.2 (NCH_2CH_3), 75.4 ($C\equiv C$), 99.4 ($C\equiv C$), 112.1 (C_β), 117.9, 130.4, 144.4, 145.7 (4 Pyr C), 135.7 (C_γ), 190.3 (C_α), 219.4 (cis-CO), 223.7 (trans-CO). FAB (MS): *m/z* (%) 487 (23) [M^+], 375 (95) [$(M - 4CO)^+$], 347 (100) [$(M - 5CO)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 502 (4.363). Anal. Calcd for $C_{26}H_{29}NO_5Cr$ (487.52): C, 64.06; H, 6.00; N, 2.87. Found: C, 63.90; H, 5.61; N, 3.01.

Pentacarbonyl[*N*-ethyl-6-(phenylethynyl)-3-hydropyridine-1,2-propadienylidene]chromium (8a). Yield: 0.42 g (99%), red solid. Mp: 112−114 °C. IR (THF): ν(CO, CCC) 2078 vw, 2003 m, 1931 vs, 1904 m cm^{-1}. ^1H NMR (400 MHz, d_6-acetone): δ 1.44 (t, $^3J_{HH} = 7.4$ Hz, 3H, NCH_2CH_3), 4.56 (q, $^3J_{HH} = 7.4$ Hz, 2H, NCH_2CH_3), 7.21−7.38 (m, 6H, Ar H + Pyr H), 8.07 (dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 2.0$ Hz, 1H, Pyr H), 8.75 (d, $^4J_{HH} = 2.1$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 14.8 (NCH_2CH_3), 55.4 (NCH_2CH_3), 83.9 ($C\equiv C$), 95.9 ($C\equiv C$), 112.9 (C_β), 116.9, 130.5, 144.0, 146.0 (4 Pyr C), 122.4, 129.6, 130.6, 132.4 (4 Ar C), 135.8 (C_γ), 192.6 (C_α), 219.3 (cis-CO), 223.8 (trans-CO). FAB (MS): *m/z* (%) 423 (17) [M^+], 367 (12) [$(M - 2CO)^+$], 339 (19) [$(M - 3CO)^+$], 311 (82) [$(M - 4CO)^+$], 283 (100) [$(M - 5CO)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 516 (4.452). Anal. Calcd for $C_{22}H_{13}NO_5Cr$ (423.35): C, 62.42; H, 3.10; N, 3.31. Found: C, 62.02; H, 3.30; N, 3.29.

Pentacarbonyl{*N*-ethyl-6-[(4-phenylethynyl)phenylethynyl]-3-hydropyridine-1,2-propadienylidene}chromium (9a). Yield: 0.37 g (71%), red solid. Mp: 99−101 °C. IR (THF): ν(CO, CCC) 2077 vw, 2001 m, 1931 vs, 1904 m cm^{-1}. ^1H NMR (400 MHz, d_6-acetone): δ 1.55 (t, $^3J_{HH} = 7.0$ Hz, 3H, NCH_2CH_3), 4.67 (q, $^3J_{HH} = 7.2$ Hz, 2H, NCH_2CH_3), 7.30−7.51 (m, 10H, 4 Ar H + Pyr H), 8.09 (dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 2.0$ Hz, 1H, Pyr H), 8.77 (d, $^4J_{HH} = 2.1$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 14.8 (NCH_2CH_3), 55.4 (NCH_2CH_3), 85.8 ($C\equiv C$), 89.3 ($C\equiv C$), 92.6 ($C\equiv C$), 95.4 ($C\equiv C$), 113.1 (C_β), 116.7, 130.7, 144.0, 146.2 (4 Pyr C), 123.3, 123.4, 125.5, 129.5, 129.7, 132.4, 132.6, 132.7 (8 Ar C), 135.9 (C_γ), 192.9 (C_α), 219.3 (cis-CO), 223.8 (trans-CO). FAB (MS): *m/z* (%) 523 (14) [M^+], 467 (8) [$(M - 2CO)^+$], 411 (100) [$(M - 4CO)^+$], 383 (84) [$(M - 5CO)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 522 (4.478). Anal. Calcd for $C_{30}H_{17}NO_5Cr$ (523.47): C, 68.84; H, 3.27; N, 2.68. Found: C, 68.42; H, 3.25; N, 2.72.

Pentacarbonyl[6-(4-ethynylphenyl)ethynyl-*N*-ethyl-3-hydropyridine-1,2-propadienylidene]chromium (10a). Yield: 0.24 g (54%), red-violet solid. Mp: 91−93 °C. IR (THF): ν(CO, CCC) 2078 vw, 2001 m, 1931 vs, 1904 m cm^{-1}. ^1H NMR (400 MHz, d_6-acetone): δ 1.55 (t, $^3J_{HH} = 7.0$ Hz, 3H, NCH_2CH_3), 3.76 (s, 1H, $C\equiv CH$), 4.66 (q, $^3J_{HH} = 7.0$ Hz, 2H, NCH_2CH_3), 7.45−7.50 (m, 5H, Ar H + Pyr H), 8.08 (dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 2.0$ Hz, 1H, Pyr H), 8.75 (d, $^4J_{HH} = 1.9$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 14.8 (NCH_2CH_3), 55.4 (NCH_2CH_3), 81.9 ($C\equiv C$), 83.4 ($C\equiv C$), 85.7 ($C\equiv C$), 95.1 ($C\equiv C$), 116.5 (C_β), 113.1, 130.6, 144.0, 146.1 (4 Pyr C), 122.7, 124.3, 133.1, 133.8 (4 Ar C), 135.8 (C_γ), 193.2 (C_α), 219.3 (cis-CO), 223.7 (trans-CO). FAB (MS): *m/z* (%) 447 (31) [M^+], 391 (26) [$(M - 2CO)^+$], 363 (29) [$(M - 3CO)^+$], 335 (71) [$(M - 4CO)^+$], 307 (100) [$(M - 5CO)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 522 (4.457). Anal. Calcd for $C_{24}H_{13}NO_5Cr$ (447.37): C, 64.44; H, 2.93; N, 3.13. Found: C, 62.91; H, 3.14; N, 2.91. Due to the reactivity of the complex, a correct elemental analysis could not be obtained.

Pentacarbonyl[*N*-ethyl-6-(ferrocenylethynyl)-3-hydropyridine-1,2-propadienylidene]chromium (11a). Yield: 0.39 g (73%), red solid. Mp: 77 °C dec. IR (THF): ν(CO, CCC) 2077 vw, 2002 m, 1930 vs, 1903 m cm^{-1}. ^1H NMR (400 MHz, d_6-acetone): δ 1.66 (t, $^3J_{HH} = 7.4$ Hz, 3H, NCH_2CH_3), 4.27 (s, 5H, Fc H), 4.38 (t, $^3J_{HH} = 1.6$ Hz, 2H, Fc H), 4.57 (t, $^3J_{HH} = 1.9$ Hz, 2H, Fc H), 4.78 (q, $^3J_{HH} = 7.4$ Hz, 2H, NCH_2CH_3), 7.54 (d, $^3J_{HH} = 8.4$ Hz, 1H, Pyr H), 8.07 (dd, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 2.0$ Hz, 1H, Pyr H), 8.75 (d, $^4J_{HH} = 2.1$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 14.9 (NCH_2CH_3), 55.3 (NCH_2CH_3), 63.9 (Fc C), 70.5 (Fc C), 70.9 (Fc C), 72.4 (Fc C), 80.2 ($C\equiv C$), 96.6 ($C\equiv C$), 112.4 (C_β), 117.9, 130.5, 144.2, 145.6 (4 Pyr C), 137.7 (C_γ), 190.1 (C_α), 219.4 (cis-CO), 223.7 (trans-CO). FAB (MS): *m/z* (%): 531 (12) [M^+], 446 (10) [$(M - 3CO)^+$], 419 (41) [$(M - 4CO)^+$], 391 (100) [$(M - 5CO)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 519 (4.424). Anal. Calcd for $C_{26}H_{17}CrFeNO_5$ (531.27): C, 58.78; H, 3.23; N, 2.64. Found: C, 58.43; H, 3.67; N, 2.64.

Pentacarbonyl{*N*-ethyl-6-[4-(ferrocenylethynyl)phenylethynyl]-3-hydropyridine-1,2-propadienylidene}chromium (12a). Yield: 0.38 g (61%), red solid. Mp: 67 °C (dec). IR (THF): ν(CO, CCC) 2077 vw, 2002 m, 1931 vs, 1904 m cm^{-1}. ^1H NMR (400 MHz, d_6-acetone): δ 1.54 (t, $^3J_{HH} = 7.0$ Hz, 3H, NCH_2CH_3), 4.13 (s, 5H, Fc H), 4.20 (t, $^3J_{HH} = 1.9$ Hz, 2H, Fc H), 4.41 (t, $^3J_{HH} = 2.0$ Hz, 2H, Fc H), 4.65 (q, $^3J_{HH} = 7.2$ Hz, 2H, NCH_2CH_3), 7.29 − 7.49 (m, 5H, 4 Ar H + Pyr H), 8.06 (dd, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 2.0$ Hz, 1H, Pyr H), 8.73 (d, $^4J_{HH} = 2.1$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 14.8 (NCH_2CH_3), 55.4 (NCH_2CH_3), 65.2 (Fc C), 70.0 (Fc C), 70.7 (Fc C), 72.2 (Fc C), 85.5 ($C\equiv C$), 85.7 ($C\equiv C$), 92.5 ($C\equiv C$), 95.6 ($C\equiv C$), 113.0 (C_β), 116.7, 130.6, 143.9, 146.0 (4 Pyr C), 121.4, 126.1, 132.3, 132.6 (4 Ar C), 135.7 (C_γ), 192.9 (C_α), 219.3 (cis-CO), 223.7 (trans-CO). FAB (MS): *m/z* (%) 629 (8) [M^+], 517 (60) [$(M - 4CO + H)^+$], 489 (100) [$(M - 5CO + H)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 520 (4.421). Anal. Calcd for $C_{34}H_{19}CrFeNO_5$ (629.37): C, 64.89; H, 3.04; N, 2.23. Found: C, 65.18; H, 3.32; N, 2.19.

Pentacarbonyl{*N*-ethyl-6-[4-(4-(ferrocenylethynyl)phenylethynyl)phenylethynyl]-3-hydropyridine-1,2-propadienylidene}-chromium (13a). Yield: 0.33 g (45%), red solid. Mp: 72 °C dec. IR (THF): ν(CO, CCC) 2078 vw, 2001 m, 1931 vs, 1904 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 1.66 (t, $^3J_{HH} = 7.4$ Hz, 3H, $\mathrm{NCH_2C}\mathit{H}_3$), 4.24 (s, 5H, Fc H), 4.32 (t, $^3J_{HH} = 1.9$ Hz, 2H, Fc H), 4.53 (t, $^3J_{HH} = 1.9$ Hz, 2H, Fc H), 4.79 (q, $^3J_{HH} = 7.4$ Hz, 2H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$), 7.33−7.63 (m, 9H, 4 Ar H + Pyr H), 8.20 (dd, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 2.0$ Hz, 1H, Pyr H), 8.89 (d, $^4J_{HH} = 2.1$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 14.7 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$), 55.5 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$), 65.7 (Fc C), 70.0 (Fc C), 70.7 (Fc C), 72.2 (Fc C), 78.0 (C≡C), 85.1 (C≡C), 90.9 (C≡C), 91.9 (C≡C), 95.4 (C≡C), 97.2 (C≡C), 113.1 (C_β), 119.9, 130.7, 143.7, 146.2 (4 Pyr C), 122.8, 125.4, 129.4, 132.2, 132.5, 132.7, 133.1, 134.9 (8 Ar C), 135.9 (C_γ), 185.0 (C_α), 219.3 (cis-CO), 223.7 (trans-CO). FAB (MS): *m/z* (%) 731 (5) [M^+], 619 (73) [$(M - 4CO)^+$], 591 (100) [$(M - 5CO)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 522 (4.529). Anal. Calcd for $C_{42}H_{25}CrFeNO_5$ (731.51): C, 68.96; H, 3.44; N, 1.91. Found: C, 68.13; H, 3.42; N, 1.76.

Pentacarbonyl[*N*-ethyl-5-(ferrocenylethynyl)-3-hydropyridine-1,2-propadienylidene]tungsten (14a). Yield: 0.32 g (60%), red solid. Mp: 111−112 °C. IR (THF): ν(CO, CCC) 2077 vw, 2009 m, 1930 vs, 1902 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 1.67 (t, $^3J_{HH} = 7.2$ Hz, 3H, $\mathrm{NCH_2C}\mathit{H}_3$), 4.36 (s, 5H, Cp), 4.53 (t, $^3J_{HH} = 7.2$ Hz, 2H, Cp), 4.78(t, $^3J_{HH} = 1.6$ Hz, 2H, Cp), 5.04 (q, $^3J_{HH} = 1.6$ Hz, 2H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$), 7.53 (d, $^3J_{HH} = 8.4$ Hz, 1H, Pyr H), 7.63 (d, $^3J_{HH} = 8.6$ Hz, 1H, Pyr H), 8.25 (t, $^3J_{HH} = 8.2$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 13.7 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$), 54.9 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$), 71.2 (Cp), 71.8 (Cp), 73.3 (Cp), 78.7 (Cp), 83.5 (C≡C), 105.4 (C≡C), 111.9 (C_β), 125.3, 129.2, 136.7, 142.2 (4 Pyr C), 138.3 (C_γ), 185.7 (C_α), 219.5 (cis-CO), 223.7 (trans-CO). FAB (MS): *m/z* (%) 531 (21) [M^+], 419 (69) [$(M - 4CO)^+$], 391 (100) [$(M - 5CO)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 524 (4.136). Anal. Calcd for $C_{26}H_{17}NO_5Cr$ (531.27): C, 58.78; H, 3.23; N, 2.64. Found: C, 58.63; H, 3.32; N, 2.54.

Pentacarbonyl(6-ethynyl-*N*-ethyl-3-hydropyridine-1,2-propadienylidene)chromium (15a). A solution of 0.4 g (1 mmol) of **6a** in 50 mL of MeOH/THF (1/1) was treated at 0 °C with 0.1 g of KF, KOH, or K_2CO_3. After the mixture was stirred for 30 min at this temperature, 20 mL of degassed water was added. The solution was extracted three times with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and filtered. The solvent was removed, and the residue was chromatographed on silica at −20 °C using mixtures of pentane and CH_2Cl_2 (1/1 to 1/3) as the eluent. Yield: 0.35 g (99%), red solid. Mp: 111 °C. IR (THF): ν(CO, CCC) 2077 vw, 2003 m, 1930 vs, 1904 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 1.53 (t, $^3J_{HH} = 7.0$ Hz, 3H, $\mathrm{NCH_2C}\mathit{H}_3$), 4.06 (s, 1H, C≡CH), 4.65 (q, $^3J_{HH} = 7.1$ Hz, 2H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$), 7.47 (d, $^3J_{HH} = 8.6$ Hz, 1H, Pyr H), 8.02 (dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 1.6$ Hz, 1H, Pyr H), 8.69 (d, $^4J_{HH} = 1.6$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 14.8 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$), 55.4 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$), 78.0 (C≡C), 85.7 (C≡C), 115.8 (C_β), 112.8, 130.6, 144.6, 146.8 (4 Pyr C), 136.3 (C_γ), 193.2 (C_α), 219.3 (cis-CO), 223.7 (trans-CO). FAB (MS): *m/z* (%) 347 (21) [M^+], 263 (17) [$(M - 3CO)^+$], 235 (81) [$(M - 4CO)^+$], 207 (100) [$(M - 5CO)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 514 (4.345). Anal. Calcd for $C_{16}H_9NO_5Cr$ (347.28): C, 55.34; H, 2.61; N, 4.03. Found: C, 55.35; H, 2.65; N, 4.04.

Pentacarbonyl{6-[dicarbonyl(η^5-cyclopentadienyl)ruthenio]-ethynyl-*N*-ethyl-3-hydropyridine-1,2-propadienylidene}-chromium (16a). A 0.02 g (10 mol %) amount of CuI and 0.33 g (1.1 mmol) of [$Cp(CO)_2RuBr$] were added at 0 °C to a solution of 0.35 g (1 mmol) of complex **15a** in 10 mL of THF/Et_3N (1/1). The solution was stirred at this temperature for 60 min. The solvent was evaporated, and the residue was chromatographed on silica at −20 °C using mixtures of pentane and CH_2Cl_2 (1/1 to 1/3) as the eluent. Yield: 0.33 g (58%), orange solid. Mp: 65 °C dec. IR (THF): ν(CC) 2114 w; ν(CO, CCC) 2078 vw, 2045 m (Ru-CO), 2009 m, 1996 m (Ru-CO), 1928 vs, 1899 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 1.49 (t, $^3J_{HH} = 7.0$ Hz, 3H, $\mathrm{NCH_2C}\mathit{H}_3$), 4.58 (q, $^3J_{HH} = 7.1$ Hz, 2H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$), 5.60 (s, 5H, Cp H), 7.31 (d, $^3J_{HH} = 8.6$ Hz, 1H, Pyr H), 7.75 (d, $^3J_{HH} = 8.6$ Hz, 1H, Pyr H), 8.30 (s, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 15.0 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$), 55.0 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$), 89.6 (Cp C), 101.3 (C≡C), 105.0 (C≡C), 110.6 (C_β), 122.2, 130.0, 144.7, 144.8 (4 Pyr C), 134.3 (C_γ), 182.7 (C_α), 198.3 (Ru−CO), 219.6 (cis-CO), 223.7 (trans-CO). FAB (MS): *m/z* (%) 569 (21) [$M + H^+$], 513 (9) [$(M - CO + H)^+$], 485 (14) [$(M - 2CO + H)^+$], 457 (100) [$(M - 4CO + H)^+$], 429 (91) [$(M - 5CO + H)^+$], 401 (28) [$(M - 6CO + H)^+$], 373 (32) [$(M - 7CO + H)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 487 (4.410). Anal. Calcd for $C_{23}H_{13}CrNO_7Ru$ (568.43): C, 48.60; H, 2.31; N, 2.46. Found: C, 48.84; H, 2.48; N, 2.63.

Pentacarbonyl{6-[dicarbonyl(η^5-pentamethylcyclopentadienyl)-ferrio]ethynyl-*N*-ethyl-3-hydropyridine-1,2-propadienylidene}-chromium (17a). A 0.02 g (10 mol %) amount of CuI and 0.36 g (1.1 mmol) of [$Cp^*(CO)_2FeBr$] were added at 0 °C to a solution of 0.35 g (1 mmol) of complex **15a** in 10 mL of THF/Et_3N (1/1), and the solution was stirred at 0 °C for 60 min. The solvent was evaporated, and the residue was chromatographed on silica at −20 °C using mixtures of pentane and CH_2Cl_2 (1/1 to 1/3) as the eluent to yield 0.26 g (38%) of a brown oil. IR (THF): ν(CC) 2095 w; ν(CO, CCC) 2077 vw, 2017 m (Fe−CO), 2009 m, 1972 m (Fe−CO), 1928 vs, 1899 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 1.60 (t, $^3J_{HH} = 7.0$ Hz, 3H, $\mathrm{NCH_2C}\mathit{H}_3$), 1.91 (s, 15H, Cp CH_3), 4.69 (q, $^3J_{HH} = 7.1$ Hz, 2H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$), 7.40 (d, $^3J_{HH} = 8.6$ Hz, 1H, Pyr H), 7.88 (d, $^3J_{HH} = 8.6$ Hz, 1H, Pyr H), 8.39 (s, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 10.1 (Cp CH_3), 15.2 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$), 55.1 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$), 99.0 (Cp C), 107.6 (C≡C), 110.6 (C_β), 125.9 (C≡C), 123.1, 130.0, 144.5, 144.8 (4 Pyr C), 133.7 (C_γ), 181.6 (C_α), 215.6 (Fe−CO), 219.9 (cis-CO), 223.9 (trans-CO). FAB (MS): *m/z* (%) 593 (20) [M^+], 481 (90) [$(M - 4CO)^+$], 453 (100) [$(M - 5CO)^+$], 397 (63) [$(M - 7CO)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 492 (4.284). $C_{28}H_{23}CrFeNO_7$ (593.34). Due to the instability of the complex, a satisfactory elemental analysis could not be obtained.

1,4-Bis{6,6′-[Pentacarbonyl(*N*-ethyl-3-hydropyridine-1,2-propadienylidene)chromium]butadiyne (18a). To a solution of 0.35 g (1 mmol) of complex **15a** in 10 mL of THF/pyridine (1/1) was added 0.20 g (1.1 mmol) of $Cu(OAc)_2$ at 0 °C. The solution was stirred at this temperature for 180 min. The solvent was evaporated, and the residue was chromatographed on silica at −20 °C using mixtures of pentane and CH_2Cl_2 (1/1 to neat CH_2Cl_2) as the eluent to yield 0.21 g (60%) of a violet solid. Mp: 50 °C dec. IR (THF): ν(CO, CCC) 2077 vw, 1993 m, 1933 vs, 1906 m cm^{-1}. ^{1}H NMR (400 MHz, d_6-acetone): δ 1.53 (t, $^3J_{HH} = 7.0$ Hz, 3H, $\mathrm{NCH_2C}\mathit{H}_3$), 4.64 (q, $^3J_{HH} = 7.1$ Hz, 2H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$), 7.49 (d, $^3J_{HH} = 8.6$ Hz, 1H, Pyr H), 8.10 (dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 2.0$ Hz, 1H, Pyr H), 8.83 (d, $^4J_{HH} = 2.1$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 14.8 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$), 55.5 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$), 78.5 (C≡C), 78.7 (C≡C), 114.7 (C_β), 114.1, 130.8, 144.2, 147.9 (4 Pyr C), 136.1 (C_γ), 198.2 (C_α), 219.1 (cis-CO), 223.8 (trans-CO). FAB (MS): *m/z* (%) 692 (11) [M^+], 636 (5) [$(M - 2CO)^+$], 552 (81) [$(M - 5CO)^+$], 412 (100) [$(M - 10CO)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 575 (4.685). Anal. Calcd for $C_{32}H_{16}N_2O_{10}Cr_2$ (692.48): C, 55.50; H, 2.33; N, 4.05. Found: C, 54.67; H, 2.75; N, 3.78.

Tetracarbonyl(diphenylferrocenylphosphane)(*N*-ethyl-3-hydropyridine-1,2-propadienylidene)chromium (19a). A solution containing 0.40 g (1 mmol) of allenylidene complex **5a** and 0.44 g (1.2 mmol) of $Ph_2P(Fc)$ in 30 mL of dry THF was irradiated at −20 °C while a slow stream of argon was passed through the solution. Irradiation was stopped when the starting compound was completely consumed (as indicated by IR spectroscopy; ca. 120 min). The solvent was removed in vacuo, and the residue was chromatographed at −20 °C on silica using mixtures of pentane and CH_2Cl_2 (1/1 to 1/3) as the eluent. A 0.41 g (62%) amount of a violet solid was obtained. Mp: 111 °C dec. IR (THF): ν(CO, CCC) 2037 w, 1968 m, 1896 vs, 1887 vs, 1857 m cm^{-1}. ^1H NMR (400 MHz, d_6-acetone): δ 1.38 (t, $^3J_{HH} = 7.4$ Hz, 3H, NCH_2CH_3), 4.04 (s, 5H, Fc H), 4.30−4.39 (m, 6H, 4Fc H + NCH_2CH_3), 7.40−7.65 (m, 11H, 10 Ar H + Pyr H), 8.09 (d, $^3J_{HH} = 8.4$ Hz, 1H, Pyr H), 8.77 (d, $^2J_{HH} = 2.1$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 16.6 (NCH_2CH_3), 55.5 (NCH_2CH_3), 71.8 (Fc C), 72.8 (d, $^3J_{PC} = 5.8$ Hz, Fc C), 76.5 (d, $^2J_{PC} = 10.5$ Hz, Fc C), 84.0 (d, $^1J_{PC} = 32.5$ Hz, Fc C), 118.4 (C_β), 119.8, 130.6, 142.4, 143.6 (4 Pyr C), 137.8 (C_γ), 129.3 (d, $^3J_{PC} = 7.7$ Hz, PAr C), 132.1 (d, $^4J_{PC} = 1.2$ Hz, PAr C), 135.7 (d, $^2J_{PC} = 18.1$ Hz, PAr C), 143.0 (d, $^1J_{PC} = 35.4$ Hz, PAr C), 206.4 (d, $^2J_{PC} = 20.7$ Hz, C_α), 225.1 (d, $^2J_{PC} = 15.5$ Hz, cis-CO), 230.8 (d, $^2J_{PC} = 11.4$ Hz, trans-CO), 231.0 (d, $^2J_{PC} = 2.9$ Hz, cis-$CO_{\text{trans to P}}$). ^{31}P NMR (162.0 MHz, d_6-acetone): δ 60.0. FAB MS: m/z (%) 666 (21) [$(M + H)^+$], 637 (15) [$(M - CO + H)^+$], 610 (48) [$(M - 2CO + H)^+$], 554 (39) [$(M - 4CO + H)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 539 (4.215). Anal. Calcd for $C_{35}H_{28}CrFeN_2O_4P$ (665.43): C, 63.18; H, 5.05; N, 2.10. Found: C, 62.86; H, 4.43; N, 2.19.

(μ-(9,10-η):(9,10-η)-[Pentacarbonyl(*N*-ethyl-6-phenylethynyl-3-hydropyridine-1,2-propadienylidene)chromium]bis(tricarbonylcobalt)(*Co*−*Co*) (20a). A solution containing 0.30 g (0.71 mmol) of **8a** and 0.24 g (0.85 mmol, 1.2 equiv) of [$Co_2(CO)_8$] in 30 mL of dry THF was stirred at ambient temperature until all of the starting compounds were completely consumed (as indicated by TLC; ca. 180 min). The solvent was removed in vacuo. The residue was chromatographed at −20 °C on silica using mixtures of pentane and CH_2Cl_2 (1/1 to 1/2) as the eluent to yield 0.41 g (58%) of a brown-violet oil. IR (THF): ν(CO, CCC) 2095 m (Co−CO), 2076 vw, 2060 m (Co−CO), 2033 m (Co−CO), 2001 m, 1930 vs, 1904 m cm^{-1}. ^1H NMR (400 MHz, d_6-acetone): δ 1.51 (t, $^3J_{HH} = 7.2$ Hz, 3H, NCH_2CH_3), 4.72 (q, $^3J_{HH} = 7.2$ Hz, 2H, NCH_2CH_3), 7.32 (m, 3H, 3 Ar H), 7.56 (m, 2H, 2 Ar H + Pyr H), 8.11 (d, $^3J_{HH} = 8.4$ Hz, 1H, Pyr H), 8.77 (d, $^4J_{HH} = 2.0$ Hz, 1H, Pyr H). ^{13}C NMR (100 MHz, d_6-acetone): δ 15.1 (NCH_2CH_3), 55.1 (NCH_2CH_3), 120.0 (C_β), 126.9, 130.9, 142.3, 142.5 (4 Pyr C), 138.1 (C_γ), 129.4, 130.0, 130.1, 135.7 (4 Ar C), 189.3 (C_α), 209.9 (CO_{Co}), 219.4 (cis-CO), 223.7 (trans-CO). FAB MS: m/z (%) 666 (21) [$(M + H)^+$], 637 (15) [$(M - CO + H)^+$], 610 (48) [$(M - 2CO + H)^+$], 554 (39) [$(M - 4CO + H)^+$]. UV/vis: λ_{max} (log ϵ) [CH_2Cl_2] 522 (4.198). $C_{28}H_{13}Co_2CrNO_{11}$ (709.27). Due to the instability of the complex, a satisfactory elemental analysis could not be obtained.

Cyclic Voltammetric and Spectroelectrochemical Measurements. Cyclic voltammograms of **11a**−**13a** were recorded using a PAR 263 instrument in CH_2Cl_2 (0.1 M [$(n\text{-}Bu)_4N]^+PF_6^-$) at 25 °C at a platinum electrode, with an SCE reference electrode and ferrocene as internal calibrant (0.460 V vs SCE). The electrochemical data of **14a** and **19a** (supporting electrolyte 0.13 M [$(n\text{-}Bu)_4N]^+PF_6^-$) were acquired with a computer-controlled EG&G Model 273 potentiostat utilizing the EG&G 250 software package. The OTTLE cell used for spectroelectrochemistry in 1,2-$C_2H_4Cl_2$ (obtained from Acros and freshly distilled from CaH_2) follows the design by Hartl et al.[46] It comprises Pt-mesh working and counter electrodes and a thin silver wire as a pseudo-reference electrode sandwiched between the CaF_2 windows of a conventional liquid IR cell. The working electrode is positioned in the center of the spectrometer beam.

Table 6. Crystallographic Data and Refinement Methods for 2a and 19a

	2a	19a
empirical formula	$C_{18}H_{11}CrNO_5$	$C_{35}H_{28}CrFeNO_4P$
M_r	373.28	665.40
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	11.502(4)	13.557(3)
b (Å)	6.147(3)	17.219(3)
c (Å)	24.670(9)	12.975(3)
α (deg)	90	90
β (deg)	101.81(3)	97.52(3)
γ (deg)	90	90
V (Å^3)	1707.3(12)	3002.9(10)
Z	4	4
cryst size (mm^3)	0.50 × 0.40 × 0.20	0.30 × 0.23 × 0.20
ρ_{calcd} (g cm^{-3})	1.452	1.472
μ (mm^{-1})	0.697	0.939
F(000)	760	1368
radiation	Mo Kα	Mo Kα
λ (Å)	0.710 73	0.710 73
T (K)	188(2)	100(2)
max 2θ (deg)	54	58.4
index range	$-7 \le h \le 14$ $-7 \le k \le 7$ $-31 \le l \le 30$	$0 \le h \le 18$ $-23 \le k \le 0$ $-17 \le l \le 17$
no. of data	4529	8016
no. of unique data	3727	8016
parameters	226	388
R1, wR2 ($I > 2\sigma(I)$)	0.0548, 0.1037	0.0530, 0.1119
R1, wR2 (all data)	0.1126, 0.1226	0.0988, 0.1235
goodness of fit on F^2	1.018	0.856

HRS Measurements of the First Hyperpolarizabilities of 11a−13a. The measurements at a wavelength of 1500 nm were carried out as described in ref 47. Instead of the third harmonic (355 nm) generated from an Nd:YAG laser with a wavelength of 1064 nm the optical parametric oscillator (OPO)[48] in use was pumped with the second harmonic (532 nm). The signal intensity at 824 nm and the fundamental at 532 nm were removed from the Idler using dichroic mirrors (HR 650-850 and HR 532), a green light, and a silicon filter (transparent >1000 nm). An additional Glan−Taylor polarizer ensured the vertical polarization of the beam into the measurement cell. Measurements were performed with 10^{-4}−10^{-6} M solutions. The validity of Beer's law was confirmed by UV/vis measurements of samples with corresponding concentrations. Disperse Red 1 (DR 1) was used as an external standard with a value of β_{1500}(DR 1) = 70 × 10^{-30} esu. This value was obtained by comparing the slopes of the reference in CH_2Cl_2 and $CHCl_3$ to obtain the ratio of β_{solute}.[49] Using the value $\beta(CHCl_3) = 80 \times 10^{-30}$ esu,[50] the hyperpolarizibility of DR 1 in CH_2Cl_2 is estimated to be 70 × 10^{-30} esu. The effect of the refractive indices of the solvents was corrected using the simple Lorentz local field.[51]

X-ray Structural Analysis of 2a and 19a. Single crystals suitable for an X-ray structural analysis (Table 6) were grown by slow diffusion of hexane into a concentrated solution of **2a** or **19a** in CH_2Cl_2 at 4 °C. The measurements were performed with a crystal mounted on a glass fiber on a Siemens *P*4 diffractometer (graphite monochromator, Mo Kα radiation, λ = 0.710 73 Å). For the data collection the Wyckoff technique was used. The structure was solved by direct methods using the SHELXTL-97 program package.[52] The positions of the hydrogen atoms were calculated by assuming ideal geometry, and their coordinates were refined together with those of the attached carbon atoms as a "riding model". All other atoms were refined anisotropically.

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Supporting Information Available: CIF files giving further details of the structure determination of complexes **2a** and **19a**, including atomic coordinates, anisotropic displacement parameters, and geometric data. This material is available free of charge via the Internet at http://pubs.acs.org.