1,3-Heterobinuclear Cyclobutenylidene Complexes with an Exocyclic C=C Bond – Synthesis, Structure, and Spectroscopic Properties

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Pentacarbonyl(allenylidene)chromium and -tungsten, $[(CO)_5M{=}C{=}C{=}CR_2]$ (M = Cr, R = $C_6H_4CH_3$-*p* (**1a**), $C_6H_4OCH_3$ (**1b**); M = W, R = $C_6H_4CH_3$-*p* (**1c**)), react with the alkynyl complexes $[Cp(CO)_2Fe{-}C{\equiv}CR']$ (R′ = *n*Bu (**2**), Ph (**4**)), $[Cp^*(CO)_2Fe{-}C{\equiv}CnBu]$ (**6**), $[Cp(CO)\{P(OMe)_3\}\text{-}Fe{-}C{\equiv}CnBu]$ (**8**) and $[Cp(PPh_3)Ni{-}C{\equiv}CnBu]$ (**10**) by cycloaddition of the C≡C bond of the alkynyl complexes to the $C_\alpha{=}C_\beta$ bond of the allenylidene ligand to give $[[(CO)_5M\doteq\overline{C\doteq C(nBu)\doteq C(C}{=}CR_2)\doteq Fe(CO)_2Cp]$ (**3a**–**c**), $[(CO)_5Cr\doteq\overline{C\doteq C\text{-}(Ph)\doteq C(C}{=}CR_2)\doteq Fe(CO)_2Cp]$ (**5**), $[(CO)_5Cr\doteq\overline{C\doteq C(nBu)\doteq C\text{-}(C}{=}CR_2)\doteq Fe(CO)_2Cp^*]$ (**7**), $[(CO)_5M\doteq\overline{C\doteq C(nBu)\doteq C(C}{=}CR_2)\doteq Fe(CO)\{P(OMe)_3\}Cp]$ (**9a**–**c**), and $[(CO)_5M\doteq\overline{C\doteq C\text{-}(nBu)\doteq C(C}{=}CR_2)\doteq Ni(PPh_3)Cp]$ (**11a**–**c**), respectively. The cycloaddition is highly selective. The spectroscopic data of these 1,3-heterobinuclear complexes indicate a delocalized π-system $[(CO)_5M\doteq C\doteq C\doteq C\doteq Y]$ (M = Cr, W; Y = $[Fe(CO)_2Cp]$, $[Fe(CO)(P\{OMe\}_3)Cp]$, $[Fe(CO)_2Cp^*]$, $[Ni(PPh_3)\text{-}Cp]$). X-ray structural analyses of the compounds **3a**, **9a**, and **11c** reveal a "butterfly" conformation of the four-membered ring. Its puckering angle is 142° (**3a**), 152° (**9a**), and 151° (**11c**). All complexes exhibit a moderate to strong negative solvatochromic behavior. The extent of the solvatochromic effect depends on $[(CO)_5M]$ and Y and considerably decreases when $C{=}CR_2$ is replaced by e.g. CMe_2.

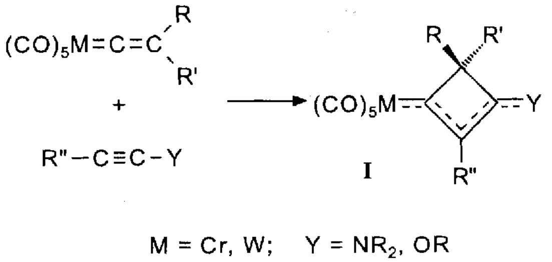
Bi- and polynuclear transition-metal complexes containing unsaturated carbon bridges recently attracted considerable interest due to their physical and chemical properties. Carbon-bridged bimetallic π-conjugated complexes of the type $[L_nMC_mM'(L')_{n'}]$ were proposed[1] as a new class of one-dimensional molecular wires[2]. Rigid rod polymers like $[L_nMC{\equiv}CXC{\equiv}C]_m$ (X = aryl) can exhibit both liquid crystalline[3] and nonlinear optical properties[4] similar to certain metal acetylides[5]. Binuclear complexes with different L_nM end groups at a conjugated π-system should exhibit second-order nonlinear optical (NLO) properties.

Related to linear C_n bridges are rigid cyclic bridges with a delocalized π-system. However, their complexes offer an advantage. By variation of the substituents at the bridging ligand a fine tuning of the magnetic, electronic and spectroscopic properties of such binuclear complexes should be possible.

Pentacarbonyl(vinylidene)chromium and -tungsten complexes react with π-donor substituted alkynes such as ynamines and alkoxyalkynes by cycloaddition of the C≡C bond of the alkyne to the C=C bond of the vinylidene ligand to form 3-amino- and 3-alkoxy-substituted cyclobutenylidene complexes (Scheme 1)[6]. In these compounds the $[(CO)_5M]$ fragment acts as the acceptor and the amino or alkoxy substituent as the donor group. Some of these complexes exhibit significant second-order nonlinear optical properties[7].

Recently, we also synthesized novel 1,3-*hetero*binuclear complexes with a cyclic C_4R_3 bridging ligand by reaction of pentacarbonyl(vinylidene)chromium complexes with alkynyl complexes of iron and nickel[8]. The properties of these 1,3-heterobinuclear complexes are strongly influenced by the substituents at both non-metal-bonded ring atoms, the sp^2- (C-2) and the sp^3-hybridized carbon atom (C-4). In addition to these complexes, a few cationic 1,3-*homo*binuclear complexes of iron[9], ruthenium[10], and rhenium[11] were prepared from alkynyl complexes and electrophiles.

Scheme 1



In this paper we report on the synthesis of the first 1,3-*hetero*binuclear cyclobutenylidene complexes with an exocyclic C=C bond at the bridging ring, the spectroscopic properties of these compounds and on the X-ray structural analyses of three representative examples.

Results and Discussion

Allenylidene complexes, $[(CO)_5M{=}C{=}C{=}CR_2]$ (M = Cr, W; R = $C_6H_4CH_3$-*p*, $C_6H_4OCH_3$-*p*), were chosen as the starting complexes. They were generated by the reaction sequence shown in Scheme 2[12].

Photolysis of $[M(CO)_6]$ (M = Cr, W) in tetrahydrofuran gave $[(CO)_5M(THF)]$. Subsequent addition of dilithiopropargylates afforded propargyl metallate derivatives. Reac-

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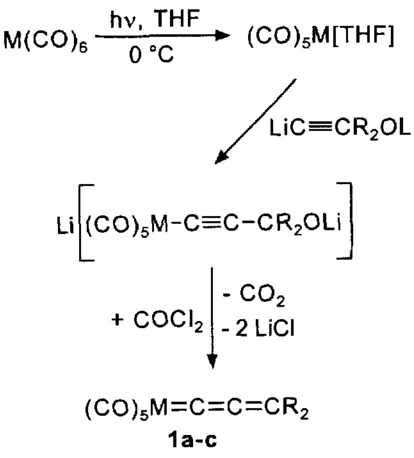
Scheme 2

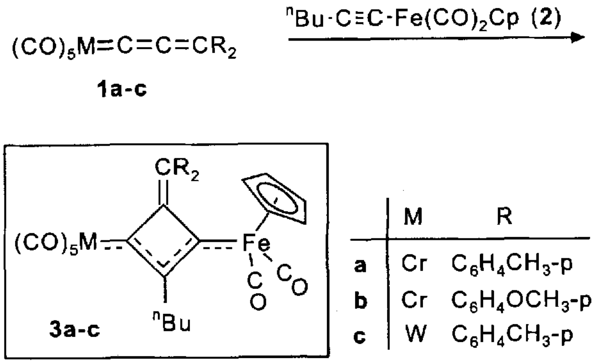


	M	R
1a	Cr	$C_6H_4CH_3$-p
1b	Cr	$C_6H_4OCH_3$-p
1c	W	$C_6H_4CH_3$-p

tion of these metallates with phosgene finally yielded the allenylidene complexes **1a**–**c**.

When solutions of these allenylidene complexes **1a**–**c** and of the alkynyl(dicarbonyl)cyclopentadienyl iron complex **2** in ether were combined at room temperature the color of the solutions changed from deep blue (**1a**, **c**) or blue-green (**1b**) to yellow. Chromatographic workup of the reaction mixtures afforded the novel cyclobutenylidene complexes **3a**–**c** (Scheme 3) in moderate yield.

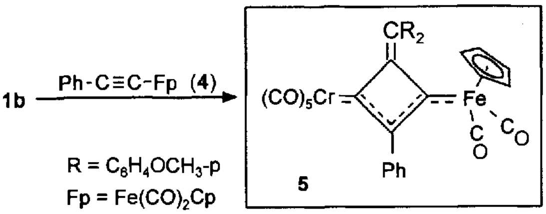
Scheme 3



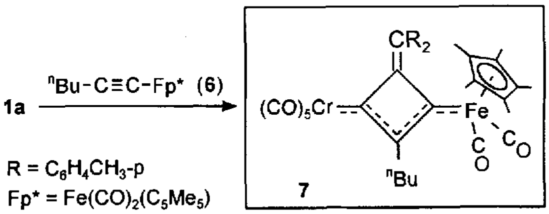
	M	R
a	Cr	$C_6H_4CH_3$-p
b	Cr	$C_6H_4OCH_3$-p
c	W	$C_6H_4CH_3$-p

The analogous reactions of **1b** with dicarbonyl(cyclopentadienyl)(phenylalkynyl)iron (**4**) and of **1a** with the pentamethylcyclopentadienyl iron complex **6** yielded the compounds **5** and **7**, respectively (Schemes 4 and 5).

Scheme 4

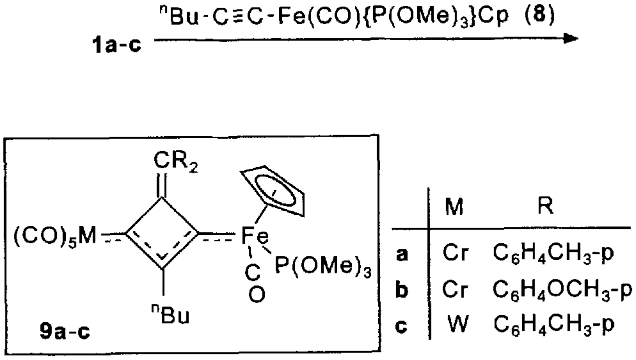


Scheme 5



Phosphite-substituted 1,3-heterobinuclear cyclobutenylidene complexes (**9a**–**c**) were obtained from **1a**–**c** and alkynyl complex **8** (Scheme 6).

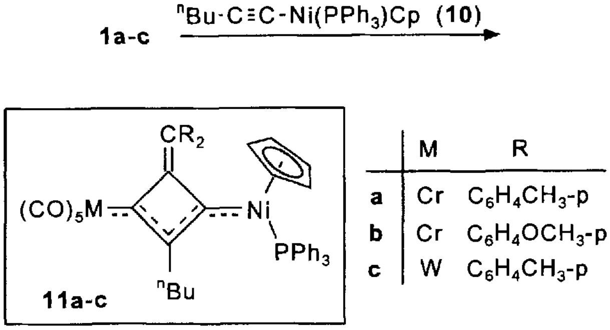
Scheme 6



	M	R
a	Cr	$C_6H_4CH_3$-p
b	Cr	$C_6H_4OCH_3$-p
c	W	$C_6H_4CH_3$-p

The formation of binuclear complexes with the $C_4R(=CR_2)$ bridging group is, however, not confined to alkynyl complexes of iron. The reaction of **1a**–**c** with [Cp(PPh$_3$)NiC≡C*n*Bu] (**10**) gave after chromatographic workup the cyclobutenylidene complexes **11a**–**c** in ca. 20% yield (Scheme 7).

Scheme 7



	M	R
a	Cr	$C_6H_4CH_3$-p
b	Cr	$C_6H_4OCH_3$-p
c	W	$C_6H_4CH_3$-p

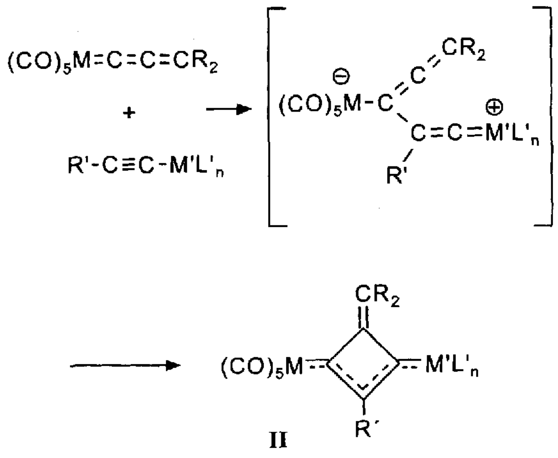
All new complexes are stable at room temperature and can easily be handled in air. They were fully characterized by microanalysis, NMR (^1H, ^{13}C, and ^{31}P), and IR spectroscopy. Additionally, the structures of the complexes **3a**, **9a**, and **11c** were established by X-ray diffraction studies (see below).

The addition of alkynyl complexes to allenylidene complexes $[(CO)_5M=C_\alpha=C_\beta=C_\gamma R_2]$ is highly selective. Only cycloaddition of the C≡C bond to the $C_\alpha=C_\beta$ bond was observed. The formation of isomeric, 1,2-dimetalated cyclobutenylidenes or of compounds derived from cycloaddition of the C≡C bond to the $C_\beta=C_\gamma$ bond of the allenylidene complexes was not detected. Ring opening of the four-membered bridging carbocycle to allenylvinylidene complexes was likewise not observed.

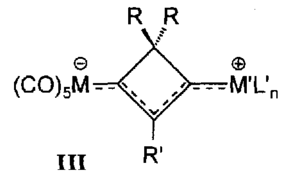
In contrast, ynamines add to the $C_\alpha=C_\beta$ as well as to the $C_\beta=C_\gamma$ bond of the allenylidene complexes **1a**–**c** to afford 3-amino-substituted cyclobutenylidene complexes $[(CO)_5M=\overline{C-C(Me)=C\{C}=C(C_6H_4R\text{-}p)_2\}-NEt_2]$ and alkenylallenylidene complexes $[(CO)_5M=C=C=C(NEt_2)-C(Me)=C(C_6H_4R\text{-}p)_2]$ (M = Cr, W; R = Me, OMe)[13]. The alkenylallenylidene complexes result from electrocyclic ring opening of the initially formed $C_\beta=C_\gamma$ cycloadducts.

The rate of cycloaddition of alkynyl complexes to the $C_\alpha=C_\beta$ bond of allenylidene complexes increases with increasing electrophilicity of the C_α atom of the allenylidene ligand (**1b** → **1a**, **1c** → **1a**) and the nucleophilicity of the C_β atom of the alkynyl group (**4** → **2**, **2** → **8**). This is consistent with a nucleophilic attack of the C_β atom of the alkynyl complex at the allenylidene C_α atom as the first reaction step. Adduct formation is followed by ring closure to the 1,3-heterodimetalated cyclobutenylidenes **II** (Scheme 8). Since it was not possible to either isolate or to spectroscopically detect intermediates, ring closure is fast compared to adduct formation.

Scheme 8



The new 1,3-heterobinuclear cyclobutenylidene complexes exhibit some unusual spectroscopic and structural features. From the ν(CO) absorption of the $[(CO)_5M]$ moiety at rather low wavenumbers it follows that the $[C_4R(=CR_2)-M'L'_n]$ residue transfers considerable electron density to this fragment. The ν(CO) spectra are similar to those of amino carbene complexes, 3-amino-substituted cyclobutenylidene complexes[6,7,13] (see **I** in Scheme 1, Y = NR_2), and 1,3-heterobinuclear cyclobutenylidene complexes **III** with a C_4R_3 bridging unit[8].



III

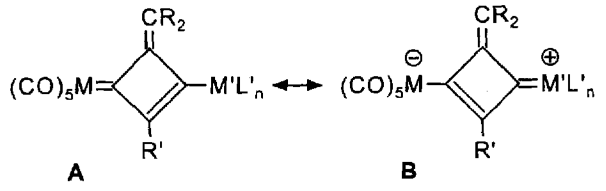
As expected substitution of $C=CR_2$ for CR_2 in **III** (**III** → **II**) only marginally influences the position of the CO stretching vibrations of $[(CO)_5M]$ which are shifted slightly to higher wavenumbers. The absorptions of the $[Cp(CO)(L)Fe]$ moiety [L = $P(OMe)_3$, CO] are also shifted to higher wavenumbers. However, the effect is more pronounced.

In agreement with the conclusions drawn from the IR spectra, the ^{13}C resonance of the chromium- or tungsten-bonded ring atom (C-1) is found in the region characteristic of amino carbene complexes. The resonance of the iron- and nickel-bonded ring atom (C-3) is observed at rather low field (δ = 191–212). With increasing back-bonding properties of the $M'L'_n$ fragment (**3c** → **9c** → **11c**) the signal of C-3 is shifted downfield.

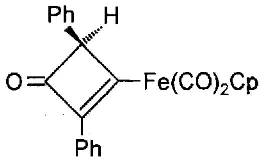
Molecular Structure of 3a, 9a, and 11c

The structures of the complexes **3a**, **9a**, and **11c** were additionally established by X-ray structural analyses (Table 1, Figures 1–3). In **3a** both C–C(*n*Bu) distances are equal, indicating that the resonance structures **A** and **B** (Scheme 9) contribute to the same extent to the overall bonding description. The distances are between the characteristic bond lengths of a $C(sp^2)-C(sp^2)$ single bond (1.46 Å) and a $C(sp^2)=C(sp^2)$ double bond (1.32 Å)[14]. The Cr(1)–C(6) distance [2.076(6) Å] is typical of a heteroatom-stabilized carbene complex[15].

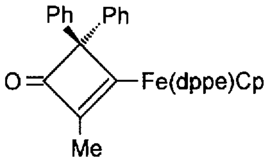
Scheme 9



An increase of the back-bonding properties of the $M'L'_n$ fragment (**3a** → **9a**) results in an elongation of the C(8)–C(9) and of the Cr(1)–C(6) bond and enhances the importance of the dipolar resonance structure **B**. Analogously to **9a**, the C(6)–C(9) bond in **11c** is shorter than the C(8)–C(9) bond. As is usually observed for carbene complexes, the carbene plane C(6),C(7),C(9) is staggered with respect to the *cis*-CO ligands, thus avoiding unfavorable steric interactions. The Fe–C(8) distance in the cyclobutenylidene complexes **3a** and **9a** is comparable to that in the cyclobut-1-en-3-one complexes **12**[16] and **13**[17].



12



13

The Fe–P(1) axis in **9a** is almost perpendicular to the plane C(7),C(8),C(9) [torsion angle C(7)–C(8)–Fe(1)–P(1) –93.6(4)°]. This conformation allows for maximum Fe→C(8) backdonation. As a consequence, the Fe–C(8) distance in **9a** is slightly shorter than that in **3a**. For the same electronic reason the C(7),C(8),C(9) plane in **11c** is almost perpendicular to the plane formed by the atoms C(8),Ni(1), and P(1) [torsion angle C(9)–C(8)–Ni(1)–P(1) –94.2(10)°] and the Ni–C(8) bond is slightly shorter than comparable bonds in related systems[18].

The most striking feature common to all complexes is the nonplanarity of the bridging ring in **3a**, **9a**, and **11c**. In contrast, the four-membered ring in 3-amino- and 3-ethoxy-substituted cyclobutenylidene complexes (Scheme 1: **I**)[6], **12**[16], and **13**[17], free cyclobut-1-en-3-ones[19], and 1,3-*homo*binuclear cyclobutenylidene complexes[11,20] is nearly planar. The puckering angle [angle between the planes formed by the atoms C(7),C(6),C(9) and C(7),C(8),C(9)] is 142° in **3a**, 152° in **9a**, and 151° in **11c**. A similar puckering was observed with other 1,3-*hetero*binuclear cyclobutenylidene complexes[8]. Obviously, exchange of an sp^2-hybridized ring-C atom ($C{=}CR_2$) for an sp^3 ring-C atom does not force the four-membered ring into planarity. As a consequence of the puckering, the transannular distance C(6)–C(8) is small in **3a** (1.926 Å), **9a** (2.009 Å) and **11c** (1.970 Å). These distances are well below the sum of the van der Waals radii. Therefore, direct electronic exchange seems possible.

Figure 1. Molecular structure of complex **3a** in the crystal (hydrogen atoms are omitted for clarity)

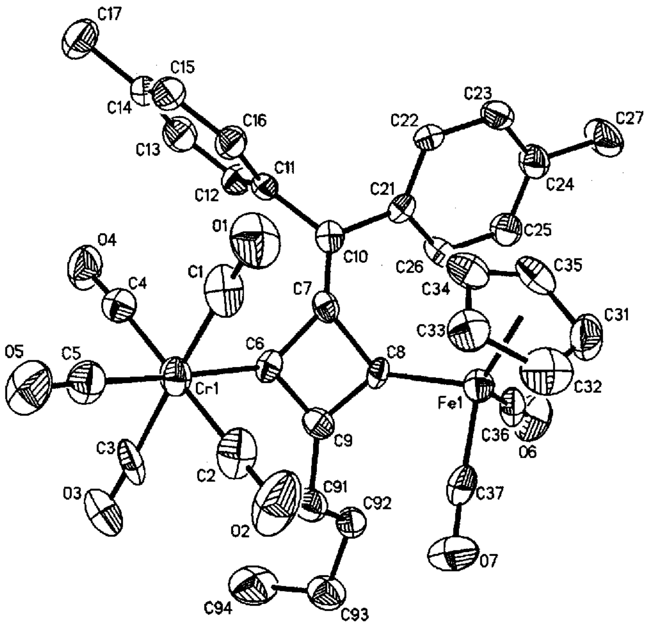
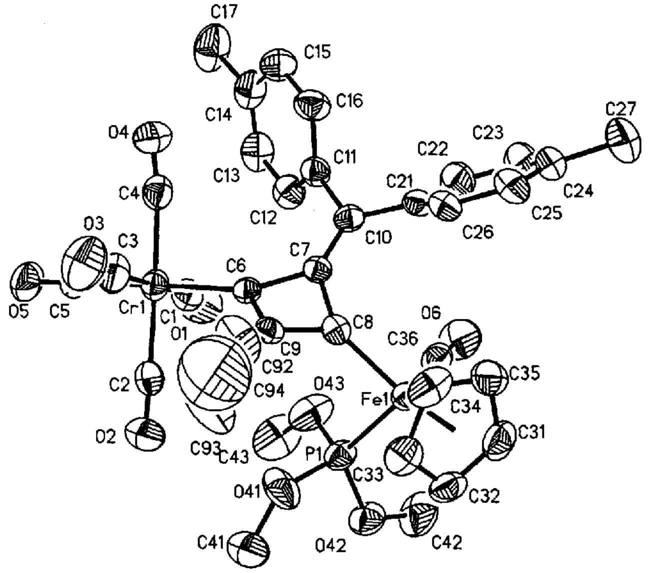


Figure 2. Molecular structure of complex **9a** in the crystal (hydrogen atoms are omitted for clarity)



Solvent Dependence of the UV/Vis Absorption

From the IR spectroscopic and the structural data a considerable contribution of the dipolar resonance structure **B** (Scheme 9) to the overall bonding description was deduced. Therefore, one might expect the 1,3-heterodinuclear cyclobutenylidene complexes to show a significant solvatochromic effect. Within a group of related polar compounds the solvatochromic effect gives important indications of the relative extent of the second-order nonlinear optical properties[21].

This expectation was confirmed by the UV/Vis spectra. The UV/Vis absorption at lowest energy is shifted to shorter wavelength when nonpolar or weakly polar solvents are replaced by more polar ones. The extent of the solvent shift $\Delta\tilde{\nu}$(pentane/DMF) is strongly influenced by the various substituents on the ring.

Substitution of CR_2 (e.g. CMe_2, CPh_2) for $C{=}CR_2$ (**II** → **III**) considerably reduces the solvatochromic effect. There is no straightforward dependence of $\Delta\tilde{\nu}$ on the back-bonding abilities of $[(CO)_5M]$ on C-1 and the $M'L'_n$ substituent at C-3. The solvent shift $\Delta\tilde{\nu}$(pentane/DMF) is reduced by replacement of $[(CO)_5Cr]$ by $[(CO)_5W]$ at C-1 in the iron-containing complexes **3** [$\Delta\tilde{\nu}$ = 3360 (**3a**), 2070 cm^{-1} (**3c**)] and **9** [$\Delta\tilde{\nu}$ = 1320 (**9a**), 940 cm^{-1} (**9c**)] and enhanced in the nickel complexes **11** [$\Delta\tilde{\nu}$ = 1730 (**11a**), 2210 cm^{-1} (**11c**)]. Substitution of $P(OMe)_3$ for a CO ligand in $[Cp(CO)_2Fe]$ (**3a** → **9a**, **3b** → **9b**) leading to an increase of the donor properties of the fragment $M'L'_n$ at C-3 reduces $\Delta\tilde{\nu}$ [4300 (**3b**), 1320 cm^{-1} (**9b**)]. The highest $\Delta\tilde{\nu}$ value observed is that for **3b**.

In summary, strongly dipolar 1,3-heterobinuclear cyclobutenylidene complexes with an exocyclic C=C bond at

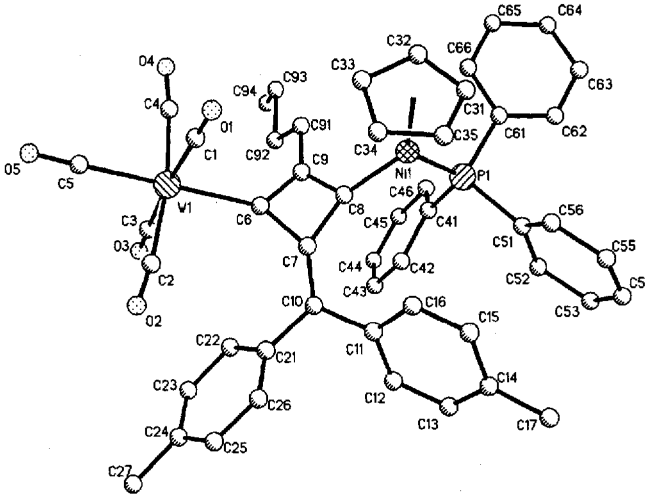


Figure 3. Molecular structure of complex **11c** in the crystal (hydrogen atoms are omitted for clarity)

Table 1. Selected bond lengths [Å] and angles [°] (standard deviations in parentheses) for **3a**, **9a**, and **11c**

	3a	**9a**	**11c**
Bond lengths [Å]			
M(1)–C(6)	2.076(6)	2.103(5)	2.210(10)
C(6)–C(7)	1.493(9)	1.513(6)	1.510(13)
C(6)–C(9)	1.408(8)	1.409(6)	1.391(16)
C(7)–C(8)	1.479(9)	1.487(6)	1.470(15)
C(8)–C(9)	1.404(9)	1.430(6)	1.418(13)
C(8)–M(2)	1.959(6)	1.907(4)	1.839(11)
C(7)–C(10)	1.327(10)	1.344(7)	1.373(14)
Bond angles [°]			
C(6)–C(7)–C(8)	80.8(5)	84.1(3)	83.0(7)
C(7)–C(6)–C(9)	90.0(5)	89.4(3)	89.8(8)
C(7)–C(8)–C(9)	90.8(5)	89.7(3)	90.5(8)
C(6)–C(9)–C(8)	86.5(5)	90.1(4)	89.2(8)

C-2 of the bridging ring are readily available by [2 + 2] cycloaddition of alkynyl complexes R′–C≡C–M′L′$_n$ to the C_α=C_β bond of allenylidene complexes [(CO)$_5$-M=C_α=C_β=C_γR$_2$]. In these complexes, the M′L′$_n$ fragment ([Cp(CO)LFe], [Cp(PPh$_3$)Ni]) acts as an electron donor and the [(CO)$_5$M] fragment as an electron acceptor. Although the ring is exclusively composed of sp^2-hybridized carbon atoms these binuclear compounds adopt a "butterfly" conformation in the solid state. A similar conformation was observed with 1,3-heterobinuclear cyclobutenylidene complexes having a C_4R_3 bridging ligand. In contrast, the ring in *homo*binuclear cyclobutenylidene complexes is planar[8]. The spectroscopic data as well as the X-ray structural analyses of representative examples indicate strong electronic interaction between the metal centers. All 1,3-heterobinuclear cyclobutenylidene complexes exhibit a pronounced negative solvatochromic effect.

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Experimental

All operations were carried out under nitrogen or 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 silica gel used for chromatography (J. T. Baker, silica gel for flash chromtography) was nitrogen-saturated. – Flash chromatography was performed at a nitrogen pressure of 1.4 bar (column length: 60 cm, column diameter: 2.5 cm). – The yields refer to analytically pure compounds and were not optimized. – Instrumentation: ^{1}H, ^{13}C and ^{31}P NMR: Bruker AC 250, Bruker WM 250, Jeol JNX 400. ^{1}H- and ^{13}C-NMR resonances are reported relative to TMS, ^{31}P-NMR resonances relative to external H_3PO_4. Unless specifically mentioned $CDCl_3$ was used as the solvent and the spectra were recorded at room temp. – IR: Biorad FTS 60 spectrophotometer. – MS: Finnigan MAT 312. – UV/Vis: Hewlett-Packard diode array spectrophotometer 8452A. – Elemental analysis: Heraeus CHN-O-RAPID. – The complexes **1a–c**[12], **2**[22], **4**[22], **6**[22], **8**[17], and **10**[23] were prepared according or analogously to literature procedures.

Pentacarbonyl[2-butyl-3-{dicarbonyl(η^5-cyclopentadienyl)ferrio}-4-{bis(p-tolyl)methylene}cyclobut-2-en-1-ylidene]chromium (**3a**): At room temp. a solution of 1.2 g (3.0 mmol) of **1a** in 30 ml of Et_2O was added to a solution of 0.77 g (3.0 mmol) of **2** in 5 ml of Et_2O. The deep blue color of the solution immediately changed to yellow. The solvent was removed in vacuo. The residue was dissolved in 20 ml of CH_2Cl_2 and the solution chromatographed at −20 °C on silica gel. With pentane/Et_2O (ratio slowly decreasing from 1:0 to 1:1) a yellow band was eluted. The solvent of the eluate was removed at −20 °C in vacuo and the residue was recrystallized from 20 ml of pentane/CH_2Cl_2 (10:1). Orange crystals. Yield: 690 mg of **3a** (33% based on **1a**), m.p. 128 °C. – IR (Et_2O): ν(CO) = 2052 cm^{-1} m, 2032 m, 1991 m, 1973 w, 1933 vs, 1921 sh. – ^{1}H NMR: δ = 0.98 (t, ^3J = 7.3 Hz, 3H, CH_3), 1.37–1.48 (m, 2H, CH_2), 1.58–1.68 (m, 2H, CH_2), 2.32 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.98 (t, 2H, ^3J = 7.6 Hz, CH_2), 4.5 (s, 5H, C_5H_5), 7.11–7.24 (m, 8H, 2 × C_6H_4). – ^{13}C NMR: δ = 13.9 (CH_3), 21.2 (CH_3), 22.7, 29.3, 29.7 (CH_2), 86.1 (C_5H_5), 113.8 (4-C), 128.9, 129.6, 130.1, 136.6, 136.7, 137.0, 138.6 (C_6H_4), 166.0 (5-C), 178.3 (2-C), 211.8 (3-C), 217.2 (Fe-CO), 217.8 (*cis*-CO), 224.4 (*trans*-CO), (1-C not found). – UV/Vis (solvent): λ_{max} (lg ε) = (pentane) 462 nm (3.85), (DMF) 400 (3.83). – MS (EI, 70 eV), *m/z* (%): 668 (2) [M$^+$], 584 (3) [M$^+$ − 3 CO], 556 (3) [M$^+$ − 4 CO], 528 (8) [M$^+$ − 5 CO], 500 (3) [M$^+$ − 6 CO], 472 (25) [M$^+$ − 7 CO], 448 (7) [M$^+$ − (CO)$_5$Cr − CO], 420 (10) [M$^+$ − (CO)$_5$Cr − 2 CO], 354 (65) [M$^+$ − (CO)$_5$Cr − 2 CO − CpH$_2$]. – $C_{35}H_{28}CrFeO_7$ (668.4): calcd. C 62.89, H 4.22; found C 62.51, H 4.23.

Pentacarbonyl[2-butyl-3-{dicarbonyl(η^5-cyclopentadienyl)ferrio}-4-{bis(p-methoxypenyl)methylene}cyclobut-2-en-1-ylidene]-chromium (**3b**): The synthesis of **3b** from 0.88 g (2.0 mmol) of **1b** in 30 ml of Et_2O and 0.52 g (2.0 mmol) of **2** in 5 ml of Et_2O (reaction time: 20 min, color change from blue-green to brown-yellow) and the purification of the products were carried out analogously to those of **1a/2**. The red fraction was collected. Recrystallization from 20 ml of pentane/CH_2Cl_2 (1:1) gave orange crystals of **3b**. Yield: 450 mg (32% based on **1b**), m.p. 129 °C. – IR (Et_2O): ν(CO) = 2051 cm^{-1} m, 2032 m, 1991 m, 1973 w, 1932 vs, 1918 s. – ^{1}H NMR: δ = 0.98 (t, ^3J = 7.2 Hz, 3H, CH_3), 1.43, 1.63 (m, 2H, CH_2), 2.99 (t, 2H, ^3J = 7.5 Hz, CH_2), 3.81 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.56 (s, 5H, C_5H_5), 6.86–7.26 (m, 8H, 2 × C_6H_4). – ^{13}C NMR: δ = 13.9 (CH_3), 22.7, 29.3, 29.8 (CH_2), 55.3, 55.4 (OCH_3), 86.2 (C_5H_5), 113.7, 113.9, 130.9, 131.2, 132.7, 134.2, 158.7, 158.9 (4-C, C_6H_4), 166.2 (5-C), 178.6 (2-C), 211.8 (3-C), 217.9 (Fe-CO), 217.8 (*cis*-CO), 224.3 (*trans*-CO), (1-C not found). – UV/Vis (solvent): λ_{max} (lg ε) = (pentane) 460 nm (3.83), (DMF) 384 (3.82). – MS (FAB, NBOH), *m/z* (%): 700 (20) [M^+], 672 (3) [M^+ – CO], 616 (100) [M^+ – 3 CO], 588 (53) [M^+ – 4 CO], 560 (97) [M^+ – 5 CO], 532 (18) [M^+ – 6 CO], 504 (88) [M^+ – 7 CO], 508 (17) [M^+ – $(CO)_5Cr$], 523 (36) [M^+ – $Fe(CO)_2Cp$]. – $C_{35}H_{28}CrFeO_9$ (700.4): calcd. C 60.01, H 4.03; found C 59.45, H 4.10.

Pentacarbonyl[2-butyl-3-{dicarbonyl(η^5-cyclopentadienyl)ferrio-4-{bis(p-tolyl)methylene}cyclobut-2-en-1-ylidene]tungsten (**3c**): The synthesis of **3c** from 1.6 g (3.0 mmol) of **1c** in 30 ml of CH_2Cl_2 and 0.77 g (3.0 mmol) of **2** in 5 ml of CH_2Cl_2 (reaction time: 20 min) and the purification of the products were carried out analogously to those of **1a/2**. With pentane/CH_2Cl_2 (ratio slowly decreasing from 1:0 to 3:2) an orange band was eluted. Recrystallization from 20 ml of pentane/CH_2Cl_2 (5:2) gave orange crystals of **3c**. Yield: 940 mg (39% based on **1c**), m.p. 135 °C (dec.). – IR (CH_2Cl_2): ν(CO) = 2059 cm^{-1} m, 2035 m, 1991 m, 1922 vs, 1895 sh. – ^1H NMR: δ = 0.99 (t, ^3J = 7.3 Hz, 3H, CH_3), 1.35–1.58 (m, 2H, CH_2), 1.61–1.67 (m, 2H, CH_2), 2.33 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.92 (t, 2H, ^3J = 7.5 Hz, CH_2), 4.53 (s, 5H, C_5H_5), 7.11–7.26 (m, 8H, 2 × C_6H_4). – ^{13}C NMR: δ = 13.9 (CH_3), 21.2 (CH_3), 22.7, 29.7, 29.9 (CH_2), 86.1 (C_5H_5), 114.1 (4-C), 128.9, 129.0, 129.6, 130.1, 136.4, 136.7, 138.4 (C_6H_4), 166.1 (5-C), 185.1 (2-C), 191.9 (3-C), 198.0 ($J_{W,C}$ = 127 Hz, *cis*-CO), 203.9 (*trans*-CO), 211.6 (Fe-CO), 212.1 (1-C). – UV/Vis (solvent): λ_{max} (lg ε) = (pentane) 448 nm (3.60), (DMF) 410 nm (3.92). – $C_{35}H_{28}FeO_7W$ (800.26): calcd. C 52.53, H 3.53; found C 52.48, H 3.61.

Pentacarbonyl[2-phenyl-3-{dicarbonyl(η^5-cyclopentadienyl)ferrio}-4-{bis(p-methoxyphenyl)methylene}cyclobut-2-en-1-ylidene]chromium (**5**): The synthesis of **5** from 0.88 g (2.0 mmol) of **1b** in 20 ml of Et_2O and 0.62 g (2.0 mmol) of **4** in 10 ml of Et_2O (reaction time: 3 h, change of color from blue-green to brown-yellow) and the purification of the products were carried out analogously to those of **1a/2**. With pentane/Et_2O/THF (ratio slowly changing from 1:0:0 to 0:2:3) an orange band was eluted. Recrystallization from 30 ml of hexane/CH_2Cl_2 (2:1) gave orange crystals of **5**. Yield: 350 mg (24% based on **1b**), m.p. 110 °C (dec.). – IR (Et_2O): ν(CO) = 2054 cm^{-1} m, 2035 m, 1995 m, 1973 w, 1931 vs, 1915 sh. – ^1H NMR: δ = 3.81 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 4.60 (s, 5H, C_5H_5), 6.87–6.98, 7.25–7.34, 7.51–7.55, 7.94–7.97 (m, 13H, 2 × C_6H_4 and C_6H_5). – ^{13}C NMR (243 K): δ = 55.3, 55.4 (OCH_3), 86.1 (C_5H_5), 113.3, 113.5, 127.9, 128.7, 130.3, 130.4, 130.5, 131.4, 132.1, 133.2, 158.3, 158.4 (4-C, C_6H_4 and C_6H_5), 168.0 (5-C), 176.7 (2-C), 204.3 (3-C), 211.3 (Fe-CO), 217.1 (*cis*-CO), 223.8 (*trans*-CO), 244.6 (1-C). – MS (FAB, NBOH), *m/z* (%): 720 (5) [M^+], 636 (17) [M^+ – 3 CO], 608 (8) [M^+ – 4 CO], 580 (17) [M^+ – 5 CO], 524 (18) [M^+ – 7 CO]. – $C_{37}H_{24}CrFeO_9$ (720.4): calcd. C 61.68, H 3.35; found C 61.41, H 3.48.

Pentacarbonyl[2-butyl-3-{dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio}-4-{bis(p-tolyl)methylene}cyclobut-2-en-1-ylidene]chromium (**7**): The synthesis of **7** from 1.0 g (2.5 mmol) of **1a** in 20 ml of CH_2Cl_2 and 0.82 g (2.5 mmol) of **6** in 15 ml of CH_2Cl_2 (reaction time: 10 min, color change from deep blue to yellow) and the purification of the products were carried out analogously to those of **1a/2**. With pentane/CH_2Cl_2 (ratio slowly decreasing from 1:0 to 3:1) and orange fraction was eluted. Recrystallization from 20 ml of pentane/CH_2Cl_2 (10:1) gave complex **7** as orange microcrystals. Yield: 680 mg (37% based on **1a**), m.p. 103 °C. – IR (Et_2O): ν(CO) = 2048 cm^{-1} m, 2014 m, 1969 m, 1929 vs, 1923 sh, 1905 sh. – ^1H NMR: δ = 1.00 (t, ^3J = 7.2 Hz, 3H, CH_3), 1.42–1.66 (m, 4H, CH_2), 1.58 (m, 15H, 5 × CH_3), 2.32 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.93 (t, 2H, ^3J = 7.7 Hz, CH_2), 7.01–7.11 (m, 8H, 2 × C_6H_4). – ^{13}C NMR (243 K): δ = 9.4 (CH_3), 13.9 (CH_3), 21.2 (CH_3), 22.9, 29.7, 30.4 (CH_2), 97.8 (C_5Me_5), 114.8 (4-C), 128.7, 129.1, 130.6, 131.0, 136.5, 138.8, 139.4 (C_6H_4), 164.2 (5-C), (2-C not found), 211.5 (3-C), 213.9 (Fe-CO), 217.9 (*cis*-CO), 224.6 (*trans*-CO), (1-C not found). – MS (FAB, NBOH), *m/z* (%): 738 (17) [M^+], 654 (48) [M^+ – 3 CO], 626 (100) [M^+ – 4 CO], 598 (37) [M^+ – 5 CO], 570 (28) [M^+ – 6 CO], 542 (71) [M^+ – 7 CO], 407 (34) [M^+ – 7 CO – C_5Me_5]. – $C_{40}H_{38}CrFeO_7$ (738.5). The complex tends to crystallize with various amounts of solvent. Therefore, correct elemental analyses could not be obtained.

Pentacarbonyl[2-butyl-3-{carbonyl(η^5-cyclopentadienyl)(trimethylphosphite)ferrio}-4-{bis(p-tolyl)methylene}cyclobut-2-en-1-ylidene]chromium (**9a**): The synthesis of **9a** from 1.2 g (3.0 mmol) of **1a** in 20 ml of Et_2O and 0.98 g (3.0 mmol) of **8** in 5 ml of Et_2O, however, at –30 °C (on addition the color of the solution immediately changed from deep blue to red) and the purification of the products were carried out analogously to those of **1a/2**. With pentane/Et_2O/THF (ratio slowly changing from 1:0:0 to 0:2:1) a dark red band was eluted. Recrystallization from 20 ml of pentane/CH_2Cl_2 (20:1) gave red crystals of **9a**. Yield: 910 mg (40% based on **1a**), m.p. 130 °C. – IR (Et_2O): ν(CO) = 2046 cm^{-1} m, 1970 m, 1926 sh, 1918 s, 1903 sh. – ^1H NMR ([D_6]acetone): δ = 1.00 (t, ^3J = 6.5 Hz, 3H, CH_3), 1.40–1.61 (m, 4H, CH_2), 2.30 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.83–3.10 (m, 2H, CH_2), 3.77 (d, ^3J = 11.2 Hz, 9H, 3 × OCH_3), 4.66 (d, *J* = 1.1 Hz, 5H, C_5H_5), 7.13–7.21 (m, 8H, 2 × C_6H_4). – ^{13}C NMR: δ = 14.0, 21.2 (CH_3), 23.2, 29.8, 30.7 (CH_2), 53.2 (d, ^2J = 7.8 Hz, OCH_3), 84.1 (C_5H_5), 114.1 (4-C), 128.1, 128.8, 130.7, 130.8, 135.4, 136.2, 138.6, 140.0 (C_6H_4), 167.4 (5-C), 2-C not found), 210.9 (3-C), 215.1 (d, ^2J = 46 Hz, Fe-CO), 218.4 (*cis*-CO), 225.2 (*trans*-CO), (1-C not found). – ^{31}P NMR: δ = 175.8 (s). – UV/Vis (solvent): λ_{max} (lg ε) = (pentane) 474 nm (3.84), (DMF) 446 nm (3.83). – MS (EI, 70 eV), *m/z* (%): 708 (5) [M^+ – 2 CO], 624 (5) [M^+ – 5 CO], 472 (38) [M^+ – 6 CO – $P(OCH_3)_3$]. – $C_{37}H_{37}CrFeO_9P$ (764.5): calcd. C 58.13, H 4.88; found C 58.04, H 4.91.

Pentacarbonyl[2-butyl-3-{carbonyl(η^5-cyclopentadienyl)(trimethylphosphite)ferrio}-4-{bis(p-methoxyphenyl)methylene}cyclobut-2-en-1-ylidene]chromium (**9b**): The synthesis of **9b** from 0.88 g (2.0 mmol) of **1b** in 20 ml of Et_2O and 0.65 g (2.0 mmol) of **8** in 20 ml of Et_2O (reaction time at –30 °C: 1 h, change of color from blue-green to yellow) and the purification of the products were carried out analogously to those of **1a/8**. With pentane/Et_2O/THF (ratio slowly changing from 1:0:0 to 0:2:1) a red fraction was eluted. Recrystallization from 30 ml of pentane/CH_2Cl_2 (2:1) gave red crystals of **9b**. Yield: 670 mg (42% based on **1b**), m.p. 135 °C. – IR (Et_2O): ν(CO) = 2045 cm^{-1} m, 1970 m, 1928 sh, 1918 s, 1905 sh. – ^1H NMR ([D_6]acetone): δ = 1.00 (t, ^3J = 6.8 Hz, 3H, CH_3), 1.46–1.60 (m, 4H, CH_2), 2.75–3.01 (m, 2H, CH_2), 3.77 (d, ^3J = 11.3 Hz, 9H, 3 × OCH_3), 3.78 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 4.71 (d, *J* = 0.7 Hz, 5H, C_5H_5), 6.86–6.94, 7.15–7.26 (m, 8H, 2 × C_6H_4). – ^{13}C NMR: δ = 14.1 (CH_3), 23.2, 29.9, 30.8 (CH_2), 53.2 (d, ^2J = 7.6 Hz, OCH_3), 55.3 (OCH_3), 84.1 (C_5H_5), 113.9 (4-C), 112.8, 113.7, 131.8, 132.1, 134.3, 135.7, 158.0, 158.8 (C_6H_4), 167.5 (5-C), (2-C not found), 210.5 (3-C), 215.1 (d, ^2J = 47 Hz, Fe-CO), 218.4 (*cis*-CO), 225.2 (*trans*-CO), (1-C not found). – ^{31}P NMR: δ = 175.7 (s). – UV/Vis (solvent): λ_{max} (lg ε) = (pentane) 474 nm, (DMF) 446 nm (3.80). – MS (FAB, NBOH), *m/z* (%): 796 (12) [M^+], 768 (1) [M^+ – CO], 740 (10) [M^+ – 2 CO], 712 (68) [M^+ – 3 CO], 684 (51) [M^+ – 4 CO], 656 (20) [M^+ – 5 CO], 628 (32) [M^+ – 6 CO], 504 (95) [M^+ – 6

CO − $P(OCH_3)_3$]. − $C_{37}H_{37}CrFeO_{11}P$ (796.5): calcd. C 55.79, H 4.68; found C 55.90, H 4.75.

Pentacarbonyl[2-butyl-3-{carbonyl(η^5-cyclopentadienyl)(trimethylphosphite)ferrio-4-{bis(p-tolyl)methylene}-cyclobut-2-en-1-ylidene]tungsten (**9c**): The synthesis of **9c** from 1.1 g (2.0 mmol) of **1c** in 20 ml of CH_2Cl_2 and 0.65 g (2.0 mmol) of **8** in 10 ml of CH_2Cl_2 (reaction temperature slowly increasing from −20°C to room temp. within 1 h, color change from blue to red) and the purification of the products (at −30°C) were carried out analogously to those of **1a/8**. With pentane/CH_2Cl_2 (ratio slowly increasing from 1:0 to 1:1) an orange fraction was eluted. Recrystallization from 25 ml of pentane/CH_2Cl_2 (4:1) gave red crystals of **9c**. Yield: 590 mg (33% based on **1c**), m.p. 142°C (dec.). − IR (CH_2Cl_2): ν(CO) = 2054 cm^{-1} m, 1967 m, 1916 s, 1883 sh. − ^1H NMR: δ = 1.00 (t, ^3J = 6.9 Hz, 3H, CH_3), 1.39−1.64 (m, 4H, CH_2), 2.33 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.69−2.75, 2.90−3.00 (m, br 2H, CH_2), 3.62 (d, ^3J = 11.3 Hz, 9H, 3 × OCH_3), 4.52 (d, J = 0.8 Hz, 5H, C_5H_5), 7.02−7.26 (m, 8H, 2 × C_6H_4). − ^{13}C NMR: δ = 14.0, 21.2 (CH_3), 22.3, 23.2, 30.7 (CH_2), 53.2 (d, ^2J = 7.9 Hz, OCH_3), 84.1 (C_5H_5), 115.2 (4-C), 128.0, 128.7, 130.7, 131.2, 135.6, 136.2, 138.1, 139.8 (C_6H_4), 167.2 (5-C), (2-C not found), 198.0 (3-C), 198.5 (^1J = 127 Hz, *cis*-CO), 204.8 ($J_{W,C}$ = 127 Hz, *trans*-CO), 210.8 (1-C), 214.8 (d, ^2J = 47 Hz, Fe-CO). − ^{31}P NMR: δ = 176.0 (s). − UV/Vis (solvent): λ_{max} (lg ε) = (pentane) 472 nm (3.86), (CH_2Cl_2) 452 nm (3.82), (DMF) 452 nm (3.82). − $C_{37}H_{37}FeO_9PW$ (896.1): calcd. C 49.55, H 4.16; found C 49.38, H 4.24.

Pentacarbonyl[2-butyl-3-{η^5-cyclopentadienyl(triphenylphosphanyl)nickelio}-4-{bis(p-tolyl)methylene}cyclobut-2-en-1-ylidene]chromium (**11a**): The synthesis of **11a** from 0.83 g (2.0 mmol) of **1a** in 30 ml of CH_2Cl_2 and 0.93 g (2.0 mmol) of **10** in 20 ml of CH_2Cl_2 (reaction time: ca. 30 min; the progress of reaction was monitored by TLC) and the purification of the products were carried out analogously to those of **1a/2**. With pentane/Et_2O (ratio slowly increasing from 1:0 to 2:3) a dark red band was eluted. Recrystallization from 20 ml of pentane/CH_2Cl_2 (10:1) gave a red microcrystals. Yield: 470 mg of **11a** (27% based on **1a**), m.p. 108°C. − IR (Et_2O): ν(CO) = 2046 cm^{-1} m, 1973 w, 1929 vs, 1910 sh. − ^1H NMR: δ = 0.73 (t, ^3J = 7.0 Hz, 3H, CH_3), 1.00−1.30 (m, 4H, CH_2), 2.33 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 2.65, 2.85 (m, 2 × 1H, C*H*H and CH*H*), 5.22 (s, 5H, C_5H_5), 6.83−7.43 (m, 23H, 2 × C_6H_4 and 3 × C_6H_5). − ^{13}C NMR: δ = 13.7 (CH_3), 21.3, 21.4 (CH_3), 22.9, 29.2, 30.6 (CH_2), 94.5 (C_5H_5), 117.0 (4-C), 128.1, 128.2, 128.3, 128.7, 129.0, 129.2, 130.2, 130.4, 131.3, 132.3, 132.9, 133.2, 133.3, 133.9, 134.0, 135.6, 136.5, 138.2 (C_6H_4 and C_6H_5), 165.1 (5-C), 187.9 (d, ^3J = 24.6 Hz, 2-C), 211.9 (3-C), 218.2 (*cis*-CO), 225.2 (*trans*-CO), 240.8 (1-C). − ^{31}P NMR: δ = 37.9 (s). − UV/Vis (solvent): λ_{max} (lg ε) = (pentane) 446 nm (3.84), (DMF) 414 nm (3.85). − MS (FAB, NBOH), *m/z* (%): 876 (4) [M^+], 792 (28) [M^+ − 3 CO], 736 (8) [M^+ − 5 CO], 671 (2) [M^+ − 5 CO − C_5H_5]. − $C_{51}H_{43}CrNiO_5P$ (877.5). The complex tends to crystallize with various amounts of solvent. Therefore, correct elemental analyses could not be obtained.

Pentacarbonyl[2-butyl-3-{η^5-cyclopentadienyl(triphenylphosphanyl)nickelio}-4-{bis(p-methoxyphenyl)methylene}cyclobut-2-en-1-ylidene]chromium (**11b**): The synthesis of **11b** from 1.1 g (2.5 mmol) of **1b** in 20 ml of CH_2Cl_2 and 1.2 g (2.5 mmol) of **10** in 20 ml of CH_2Cl_2 (reaction time: ca. 30 min; the progress of reaction was monitored by TLC) and the purification of the products were carried out analogously to those of **1a/2**. With pentane/Et_2O (ratio slowly increasing from 1:0 to 2:3) a red band was eluted. Recrystallization from 20 ml of pentane/CH_2Cl_2 (7:1) gave red crystals. Yield: 570 mg of **11b** (25% based on **1b**), m.p. 127°C. − IR (Et_2O): ν(CO) = 2046 cm^{-1} m, 1971 w, 1929 vs, 1913 s. − ^1H NMR: δ = 0.74 (t, ^3J = 7.2 Hz, 3H, CH_3), 1.14−1.25 (m, 4H, CH_2), 2.63, 2.85 (m, 1H, C*H*H and CH*H*), 3.77, 3.80 (s, 3H, OCH_3), 5.20 (s, 5H, C_5H_5), 6.58−7.60 (m, 23H, 2 × C_6H_4 and 3 × C_6H_5). − ^{13}C NMR: δ = 13.7 (CH_3), 22.9, 29.1, 30.6 (CH_2), 54.9, 55.2 (OCH_3), 94.4 (C_5H_5), 112.8, 113.4 (C_6H_4), 117.4 (4-C), 128.1, 128.3, 128.7, 128.8, 129.0, 129.2, 130.4, 131.3, 132.0, 132.6, 132.8, 133.1, 133.2, 133.8, 134.0 (C_6H_4), (5-C not found), 189.4 (d, ^3J = 25.3 Hz, 2-C), 211.2 (3-C), 218.2 (*cis*-CO), 225.2 (*trans*-CO), 241.8 (1-C). − ^{31}P NMR: δ = 38.2 (s). − UV/Vis (solvent): λ_{max} (lg ε) = (pentane) 450 nm (3.89), (DMF) 418 nm (3.94). − MS (FAB, NBOH), *m/z* (%): 908 (2) [M^+], 824 (28) [M^+ − 3 CO], 768 (11) [M^+ − 5 CO]. − $C_{51}H_{43}CrNiO_7P$ (909.6): calcd. C 67.34, H 4.77; found C 67.41, H 5.01.

Pentacarbonyl[2-butyl-3-{η^5-cyclopentadienyl(triphenylphosphanyl)nickelio}-4-{bis(p-tolyl)methylene}cyclobut-2-en-1-ylidene]tungsten (**11c**): The synthesis of **11c** from 1.6 g (3.0 mmol) of **1c** in 30 ml of CH_2Cl_2 and 1.40 g (3.0 mmol) of **10** in 20 ml of CH_2Cl_2 (reaction time: 20 min) and the purification of the products were carried out analogously to those of **1a/10**. With pentane/Et_2O (ratio slowly increasing from 1:0 to 1:1) an orange band was eluted. Recrystallization from 20 ml of pentane/CH_2Cl_2 (10:1) gave dark red crystals of **11c**. Yield 390 mg (13% based on **1c**), m.p. 110°C (dec.). − IR (CH_2Cl_2): ν(CO) = 2055 cm^{-1} m, 1975 w, 1918 vs, 1875 sh. − ^1H NMR (CD_2Cl_2, 233 K): δ = 0.71 (t, ^3J = 6.9 Hz, 3H, CH_3), 1.21−1.44 (m, 4H, CH_2), 2.18 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.40−2.50, 2.65−2.75 (m, 2 × 1H, C*H*H and CH*H*), 5.22 (s, 5H, C_5H_5), 6.83−7.43 (m, 23H, 2 × C_6H_4 and 3 × C_6H_5). − ^{13}C NMR (CD_2Cl_2, 233 K): δ = 13.9 (CH_3), 21.3, 21.5 (CH_3), 22.7, 29.5, 31.3 (CH_2), 94.9 (C_5H_5), 117.0 (4-C), 128.6, 128.7, 129.0, 130.6, 130.9, 131.5, 132.4, 133.1, 133.6, 133.8, 136.4, 136.8, 138.2, 138.4 (C_6H_4 and C_6H_5), 165.4 (5-C), 195.5 (d, ^3J = 24.2 Hz, 2-C), 199.0 ($J_{W,C}$ = 127 Hz, *cis*-CO), 204.8 (*trans*-CO), 210.0 (d, ^2J = 3.2 Hz, 3-C), 212.2 (d, ^4J = 2.9 Hz, 1-C). − ^{31}P NMR: δ = 38.3 (s). − UV/Vis (solvent): λ_{max} (lg ε) = (pentane) 434 nm (4.01), (DMF) 396 nm (3.94). − $C_{51}H_{43}NiO_5PW$ (1009.4): calcd. C 60.68, H 4.29; found C 60.54, H 4.57.

X-ray Structural Analyses of **3a**, **9a**, *and* **11c**

3a: $C_{35}H_{28}CrFeO_7$ (668.4), crystal size 0.1 × 0.2 × 0.2 mm (obtained from pentane/CH_2Cl_2, 10:1), monoclinic, $P2_1/n$, a = 13.467(4), b = 11.519(4), c = 20.625(9) Å, β = 102.99(3)°, V = 3118(2) $Å_3$, Z = 4, d_{calcd} = 1.424 g cm^{-3}, μ(Mo-K_α) = 0.851 mm^{-1}, F(000) = 1376; Wyckoff scan 4° < 2Θ < 48°, scan rate variable 2.0−29.3° min^{-1} in ω; $\Delta\omega$ = 1.40°, temp. 241 K, 10271 reflections collected, 4908 independent reflections, 2931 reflections with $F > 3.0\sigma(F)$; 397 refined parameters; R = 0.069, R_w = 0.047. Largest difference peak (hole): +0.61 e $Å^{-3}$ (−0.55 e $Å^{-3}$). − **9a**: $C_{37}H_{37}CrFeO_9P$ (764.5), crystal size 0.3 × 0.3 × 0.3 mm (obtained from pentane/CH_2Cl_2, 20:1), monoclinic, $P2_1/n$, a = 11.045(4), b = 19.118(7), c = 17.923(7) Å, β = 103.27(3)°, V = 3684(2) $Å^3$, Z = 4, d_{calcd} = 1.378 g cm^{-3}, μ(Mo-K_α) = 0.773 mm^{-1}, F(000) = 1584; Wyckoff scan 4° < 2Θ < 54°, scan rate variable 2.0−29.3° min^{-1} in ω; $\Delta\omega$ = 1.40°, temp. 253 K, 8707 reflections collected, 8027 independent reflections, 4463 reflections with $F > 4.0\sigma(F)$; 442 refined parameters; R = 0.055, R_w = 0.052. Largest difference peak (hole): +0.59 e $Å^{-3}$ (−0.49 e $Å^{-3}$). − **11c**: $C_{51}H_{43}NiO_5PW$ (1009.4), crystal size 0.3 × 0.3 × 0.3 mm (obtained from pentane/CH_2Cl_2, 7:1), monoclinic, $P2_1/n$, a = 13.466(2), b = 11.164(2), c = 33.685(6) Å, β = 100.10(1)°, V = 4987.0(15) $Å^3$, Z = 4, d_{calcd} = 1.344 g cm^{-3}, μ(Mo-K_α) = 2.805 mm^{-1}, F(000) = 2024; Wyckoff scan 4° < 2Θ < 48°, scan rate variable 4.0−30.0° min^{-1} in ω; $\Delta\omega$ = 1.40°, temp. 228 K, 11941 reflections collected, 10887 independent reflections, 6469 reflections with $F > 4.0\sigma(F)$; 527 refined parameters; $R = 0.067$, $R_w = 0.074$. Largest difference peak (hole): $+1.95$ e Å^{-3} (-1.76 e Å^{-3}). A semi-empirical absorption correction was carried out (ψ scans with 10 reflections). Min/max transmission: 0.312/0.459. – Data were collected with a crystal mounted in a glass capillary on a Siemens R3m/V (**3a**, **9a**) or Siemens P4 (**11c**) diffractometer (graphite monochromator, Mo-K_α radiation, $\lambda = 0.71073$ Å). The structures were solved by Patterson methods and refined by full-matrix least-squares techniques (Siemens SHELXTL PLUS program package). The positions of the hydrogen atoms were calculated by assuming ideal geometries ($d_{C-H} = 0.96$ Å) and their coordinates were refined together with the attached C atoms as "riding models". The butyl group in **11c** is disordered. In the present model, the ultimate refinement was performed with bond length restraints for C(92)–C(93) and C(93)–C(94). C(94) was refined with fixed isotropic U. Complete lists of atom coordinates and their thermal parameters were deposited[24].

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