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Synthesis and Crystal Structure of Novel 1,3-Heterobinuclear Complexes with an Unusual Cyclic C_4R_3 Bridging Ligand

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Pentacarbonyl(dimethylvinylidene)chromium, $[(CO)_5Cr{=}C{=}CMe_2]$ (**1**), reacts with the alkynyl complexes $[Cp(CO)_2FeC{\equiv}CR]$ (**4a**−**e**; R = ^nBu (**a**), Me (**b**), Ph (**c**), $C_6H_4NO_2$-*p* (**d**), COOMe (**e**)), $[Cp(CO)\{P(OMe)_3\}FeC{\equiv}C^nBu]$ (**6**), $[Cp(CO)\{PPh_3\}FeC{\equiv}C^nBu]$ (**8**), and $[Cp(PEt_3)NiC{\equiv}C^nBu]$ (**19**) by cycloaddition of the C≡C bond of the alkynyl complexes to the C═C bond of **1** to give $[(CO)_5Cr\mathrel{\overset{-\,-}{-}}\overline{C\mathrel{\overset{-\,-}{-}}CR\mathrel{\overset{-\,-}{-}}C(C}Me_2)\mathrel{\overset{-\,-}{-}}Fe(CO)_2Cp]$ (**5a**−**e**), $[(CO)_5Cr\mathrel{\overset{-\,-}{-}}\overline{C\mathrel{\overset{-\,-}{-}}C(^nBu)\mathrel{\overset{-\,-}{-}}C(C}Me_2)\mathrel{\overset{-\,-}{-}}Fe(CO)\{P(OMe)_3\}Cp]$ (**7**), $[(CO)_5Cr\mathrel{\overset{-\,-}{-}}\overline{C\mathrel{\overset{-\,-}{-}}C(^nBu)\mathrel{\overset{-\,-}{-}}C(C}Me_2)\mathrel{\overset{-\,-}{-}}Fe(CO)\{PPh_3\}Cp]$ (**9**), and $[(CO)_5Cr\mathrel{\overset{-\,-}{-}}\overline{C\mathrel{\overset{-\,-}{-}}C(^nBu)\mathrel{\overset{-\,-}{-}}C(C}Me_2)\mathrel{\overset{-\,-}{-}}Ni(PEt_3)Cp]$ (**20**), respectively. The analogous reaction of $[(CO)_5Cr{=}C{=}C(CH_2)_5]$ (**2**) with **4a** and **6** affords complexes with a spirocyclic bridging ligand: $[(CO)_5Cr\mathrel{\overset{-\,-}{-}}\overline{C\mathrel{\overset{-\,-}{-}}C(^nBu)\mathrel{\overset{-\,-}{-}}C\{C}(CH_2)_5\}\mathrel{\overset{-\,-}{-}}Fe(CO)_2Cp]$ (**10**) and $[(CO)_5Cr\mathrel{\overset{-\,-}{-}}\overline{C\mathrel{\overset{-\,-}{-}}C(^nBu)\mathrel{\overset{-\,-}{-}}C\{C}(CH_2)_5\}\mathrel{\overset{-\,-}{-}}Fe(CO)\{P(OMe)_3\}Cp]$ (**11**). Cycloaddition of **4a** to $[(CO)_5Cr{=}C{=}CPh_2]$ (**3**) yields $[(CO)_5Cr\mathrel{\overset{-\,-}{-}}\overline{C\mathrel{\overset{-\,-}{-}}C(^nBu)\mathrel{\overset{-\,-}{-}}C(C}Ph_2)\mathrel{\overset{-\,-}{-}}Fe(CO)_2Cp]$ (**12**). The spectroscopic data of these novel 1,3-heterobinuclear complexes indicate the delocalized π-system $Cr\mathrel{\overset{-\,-}{-}}C\mathrel{\overset{-\,-}{-}}C\mathrel{\overset{-\,-}{-}}C\mathrel{\overset{-\,-}{-}}M$ (M = Fe, Ni). X-ray structural analyses of the compounds **5e**, **10**, and **11** reveal a "butterfly" conformation. The puckering angle of the four-membered ring is 160.0° (**5e**), 143.9° (**10**), and 144.9° (**11**). Both $C(sp^2)-C(sp^2)$ bonds are almost equal in length. All complexes exhibit negative solvatochromic behavior. The extent of the solvatochromic effect is strongly influenced by the substituents at C-2 and C-4 of the ring.

Introduction

Bi- and polynuclear transition-metal complexes with unsaturated carbon bridges recently attracted considerable interest due to their physical and chemical properties.[1] Bimetallic complexes with π-conjugated carbon chains, $L_nMC_mM'(L')_n$, have been proposed as a new class of one-dimensional molecular wires.[2] Binuclear complexes with different L_nM end groups at a conjugated π-system should exhibit second-order nonlinear optical (NLO) properties.[3] The magnetic, electronic, and spectroscopic properties of such binuclear species could easily be influenced due to the large variety of transition-metal−ligand fragments available (variation of the metal, the ligand sphere, and the oxidation state). Therefore, such binuclear species are attractive synthetic goals.

Related to linear C_m bridges are rigid cyclic bridges with a delocalized π-system connecting the metals. Such compounds offer an advantage. Varying the substituents at the bridging ligand should allow a fine-tuning of the electronic communication between the metal centers.

Recently we observed that 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).[4] These compounds may be regarded as push−pull π-systems in which 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.[5]

The formation of cyclobutenylidene complexes not stabilized by π-donor substituents has also been observed or proposed in a few cases. Cationic cyclobutenylidene complexes have been obtained from the cycloaddition of phenylpropyne to $[Cp(CO)LFe{=}C{=}CH_2]^+$ (L = PPh_3, $P(OMe)_3$).[6] The reaction of $HC{\equiv}CCOOMe$ with photogenerated $[(CO)_5Cr\{OEt_2\}]$ also produced a cy-

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[1] For example: (a) Maatta, E. A.; Devore, D. D. *Angew. Chem.* **1988**, *100*, 583; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 569. (b) Chisholm, M. H. *Angew. Chem.* 1991, *103*, 690; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 673. (c) Diederich, F.; Rubin, Y. *Angew. Chem.* **1992**, *104*, 1123; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101. (d) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem.* **1993**, *105*, 969; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923. (e) Lang, H. *Angew. Chem.* **1994**, *106*, 569; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547. (f) Irwin, M. J.; Jia, G.; Payne, N. C.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 51 and literature cited therein.

[2] See, for example: (a) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem.* **1994**, *106*, 1445; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360. (b) Bartik, T.; Bartik, B.; Brady, M.; Dembinski, R.; Gladysz, J. A. *Angew. Chem.* **1996**, *108*, 467; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 414.

[3] See, for example: (a) *Inorganic Materials*; Bruce, D. W., O'Hare, D., Eds.; Wiley: Chichester, U.K., 1992. (b) *Inorganic and Organometallic Polymers II: Advanced Materials and Intermediates*; ACS Symposium Series 572; Wisian-Neilson, P., Allcock, H. R., Wynne, K. J., Eds.; American Chemical Society: Washington, D.C., 1994.

[4] Fischer, H.; Podschadly, O.; Früh, A.; Troll, C.; Stumpf, R.; Schlageter, A. *Chem. Ber.* **1992**, *125*, 2667.

[5] Fischer, H.; Podschadly, O.; Herminghaus, S., unpublished results.

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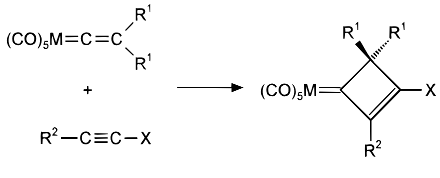
Scheme 1



M = Cr, W; X = NR$_2$, OR

clobutenylidene complex in addition to a vinylvinylidene complex and the alkyne complex [(CO)$_5$Cr(HC≡CCOOMe)].[7] Both the cyclobutenylidene complex and the vinylvinylidene complex were proposed to arise via intermediacy of the vinylidene complex [(CO)$_5$Cr=C=C(H)COOMe]. A cyclobutenylidene complex was suggested as a key intermediate in the insertion of the C≡C bond of MeOOCC≡CCOOMe into the C$_\alpha$=C$_\beta$ bond of [dppe(CO)$_3$W=C=C(H)Ph] to form a vinylvinylidene complex.[8] The vinylvinylidene complex was proposed to result from the ring opening of the cyclobutenylidene intermediate.

Transition metal alkynyl complexes, L$_n$MC≡CR, are related to the π-donor-substituted alkynes XC$_\alpha$≡C$_\beta$R (X = NR$_2$, OR). In both cases, the HOMO is mainly localized at the terminal C atom (C$_\beta$).[9] Hence, electrophiles have been observed to add at the C$_\beta$ atom of alkynyl complexes to give vinylidene complexes.[10] A suitable combination of vinylidene and alkynyl complexes should afford 1,3-bimetalated cyclic C$_4$R$_3$ compounds.

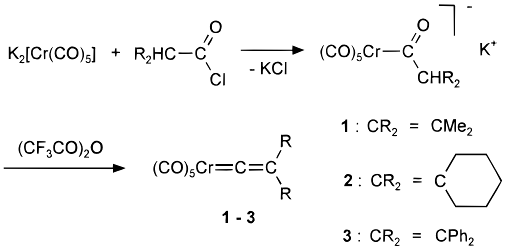
A few cationic 1,3-homobimetallic complexes of iron,[11] ruthenium,[12] and rhenium[13] have been prepared from alkynyl complexes and electrophiles. The formation of a cationic vinylidene complex as an intermediate was proposed which then adds the alkynyl complex to form the bimetallic species.

We now report on the synthesis of the first heterobimetallic cyclobutenylidene complexes and their spectroscopic and unusual structural properties.

Results and Discussion

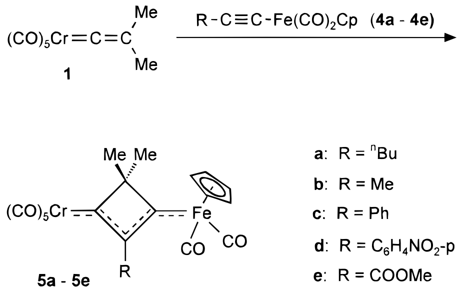
Generation of the Vinylidene Complexes (CO)$_5$Cr=C=CR$_2$ (1−3). The starting vinylidene complexes **1**−**3** were generated by the reaction sequence shown in eqs 1 and 2. Reduction of Cr(CO)$_6$ with potassium−graphite (C$_8$K) laminate in THF at 0 °C gave K$_2$[Cr(CO)$_5$] (eq 1).[14] Reaction of K$_2$[Cr(CO)$_5$] with the corresponding acyl chlorides (isobutyryl chloride, cyclohexane carbonyl chloride, or diphenylacetyl chloride) afforded potassium acyl(pentacarbonyl)chromates analogously to a method described by Semmelhack et al.[15] Reaction of these acyl(pentacarbonyl)chromates with trifluoroacetic anhydride in CH$_2$Cl$_2$ at −78 °C finally yielded the vinylidene complexes **1**−**3** (eq 2).[16] By an analogous procedure, cationic vinylidene complexes of iron have been prepared from acyl complexes by Hughes et al.[17] The vinylidene complexes are very unstable and readily decompose in solution at room temperature. Therefore, they were usually not isolated but only characterized by their ν(CO) spectra. The solutions were then immediately employed in subsequent reactions with alkynyl complexes.

$$\mathrm{Cr(CO)_6} \xrightarrow{\mathrm{C_8K}} \mathrm{K_2[Cr(CO)_5]} \qquad (1)$$



(2)

Reactions of the Pentacarbonyl(vinylidene)chromium Complexes 1−3 with Alkynyliron Complexes. When solutions of the alkynyldicarbonylcyclopentadienyliron complexes **4a**−**e** and of the vinylidene complex **1** in dichloromethane were combined at −60 °C and then warmed to room temperature, the color of the solutions changed within ca. 15 min from green to yellow or red. Chromatographic workup of the reaction mixture afforded the novel heterobimetallic cyclobutenylidene complexes **5a**−**e** (eq 3) in moderate yields.



(3)

Analogously, the trimethyl phosphite and triphenylphosphine substituted complexes **7** and **9** were obtained from **1** and [Cp(CO){P(OMe)$_3$}FeC≡C^{n}Bu] (**6**) and [Cp(CO){PPh$_3$}FeC≡C^{n}Bu] (**8**), respectively (eq 4).

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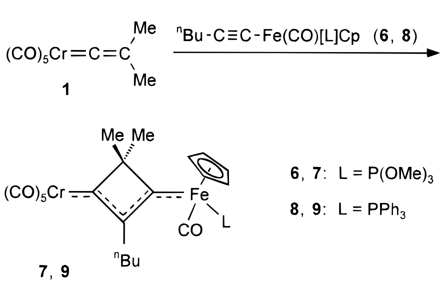
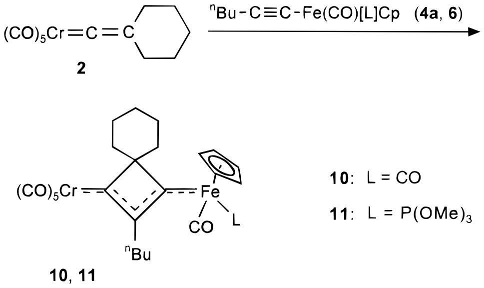
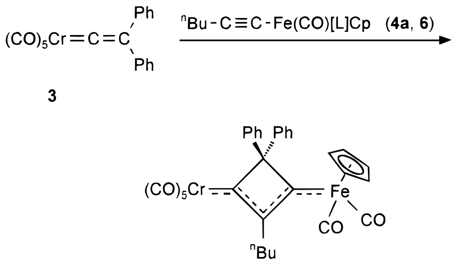


(4)

The reaction of the pentamethylenevinylidene complex **2** with the alkynyliron complexes **4a** and **6** afforded complexes with a spirocyclic bridging ligand (**10** and **11**; eq 5), and the reaction of the diphenylvinylidene complex **3** with the alkynyl complex **4a** gave the corresponding diphenyl-substituted compound **12** (eq 6).



(5)



(6)

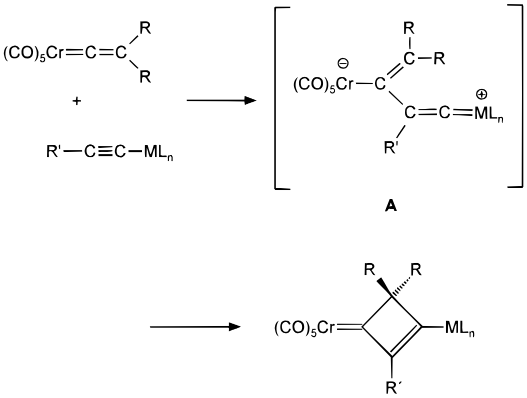
12

The new complexes which are formed by cycloaddition of the C≡C bond of the alkynyl complexes to the C=C bond of the vinylidene complexes constitute the first examples of *hetero*bimetallic cyclobutenylidene complexes. They are stable at room temperature and can easily be handled in air. They were characterized by microanalysis and NMR (^1H, ^{13}C, ^{31}P) and IR spectroscopy; additionally, the structures of the complexes **5e**, **10**, and **11** were determined by X-ray analyses (see below).

The cycloaddition is highly regioselective. The formation of isomeric, 1,2-bimetalated cyclobutenylidenes has not been observed. Vinylvinylidene complexes resulting from an opening of the four-membered ring have likewise not been detected.

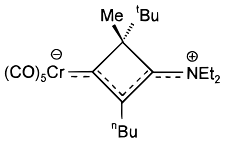
The reaction presumably takes place in a stepwise fashion, although it was not possible to either isolate intermediates or detect them spectroscopically. Nucleophilic addition of the β-carbon atom of the alkynyl complex to the vinylidene C_α atom is followed by ring closure to form the four-membered ring (Scheme 2). The formation of the first 1,3-homobinuclear cyclobutenylidene complexes $[Cp(CO)_2Fe{\cdots}\overline{C{\cdots}CPh{\cdots}C}[C(E)Ph]{\cdots}Fe(CO)_2Cp]^+$ from [Cp(CO)$_2$FeC≡CPh] and electrophiles E^+ (E = H, Me) also was suggested to proceed by a stepwise cycloaddition.[11a] Addition of E^+ to the C_β atom of [Cp(CO)$_2$FeC≡CPh] affords the cationic vinylidene complexes $[Cp(CO)_2Fe{=}C{=}C(E)Ph]^+$. Subsequent reaction with a second molecule of [Cp(CO)$_2$FeC≡CPh] finally gives, via an adduct analogous to **A** in Scheme 2, the binuclear complexes.

Scheme 2



Similar [2 + 2] cycloaddition of imines to the C=C bond of vinylidene complexes of iron,[18,19] rhenium,[20] manganese,[20] chromium,[19,21] and tungsten[22] have been reported. A stepwise mechanism was suggested. Two complexes related to the proposed intermediate **A** (Scheme 2) have been isolated.[19b,22]

The cyclobutenylidene complexes **5**, **10**, and **11** exhibit some unusual spectroscopic and structural features. From the ν(CO) absorptions of the [(CO)$_5$Cr] fragment at low wavenumbers a considerable transfer of electron density from [C_4R_3—FeL$_2$Cp] to the [(CO)$_5$Cr] fragment can be deduced. The ν(CO) spectra are similar to those of aminocarbene complexes (e.g. [(CO)$_5$Cr=C(NHMe)-Me][23]) and 3-amino-substituted cyclobutenylidene complexes[4,5] such as **13**.[4]



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Obviously, the [C_4R_3—FeL$_2$Cp] group is a very strong donor ligand and the donor properties of the [FeL$_2$Cp] fragment are similar to those of NR_2. In turn, the ν(CO) absorptions of the [Fe(CO)$_2$Cp] moiety in **5a**–**e**, **10**, and **12** are similar to those of the cyclobut-1-en-3-one iron complex **14**, indicating the electronic similarities of [(CO)$_5$Cr] and substituents as ligands in these binuclear complexes.

As expected, all ν(CO) absorptions shift toward smaller wavenumbers when the ability of the substituent at C-2 of the ring to donate electron density (COOMe, C_6H_4-NO_2-*p*, Ph, Me, ^{n}Bu) increases.

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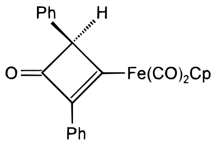
Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 5e, 10, and 11

	5e	10	11
Bond Lengths			
Cr(1)−C(5)	1.886(3)	1.887(5)	1.864(4)
Cr(1)−C(6)	2.010(3)	2.093(4)	2.109(3)
C(6)−C(7)	1.558(4)	1.569(5)	1.560(4)
C(7)−C(8)	1.541(4)	1.531(5)	1.539(5)
C(6)−C(9)	1.419(4)	1.409(5)	1.402(5)
C(8)−C(9)	1.385(4)	1.384(5)	1.388(4)
C(8)−Fe(1)	1.923(3)	1.937(4)	1.944(3)
Fe(1)−C(36)	1.772(3)	1.775(5)	1.739(3)
C(9)−C(91)	1.483(4)	1.493(5)	1.496(5)
Bond Angles			
Cr(1)−C(6)−C(7)	132.9(2)	137.0(3)	137.4(3)
C(6)−C(7)−C(8)	82.7(2)	77.0(3)	77.0(2)
Cr(1)−C(6)−C(9)	137.7(2)	130.0(3)	129.0(2)
C(7)−C(6)−C(9)	89.0(2)	91.2(3)	92.0(3)
C(7)−C(8)−C(9)	91.0(2)	93.8(3)	93.4(2)
C(7)−C(8)−Fe(1)	131.7(2)	132.5(3)	130.8(2)
C(9)−C(8)−Fe(1)	137.1(2)	132.0(3)	133.2(2)
C(6)−C(9)−C(8)	93.8(2)	87.4(3)	87.6(3)
C(8)−Fe(1)−C(36)	92.7(1)	93.2(2)	93.7(1)
Torsion Angles			
C(1)−Cr(1)−C(6)−C(7)	−137.4(3)	−34.3(4)	−33.9(3)
Fe(1)−C(8)−C(9)−C(91)	10.6(5)	−22.5(7)	−28.5(5)
C(7)−C(8)−Fe(1)−C(36)	−142.8(2)	−36.5(4)	−42.5(3)



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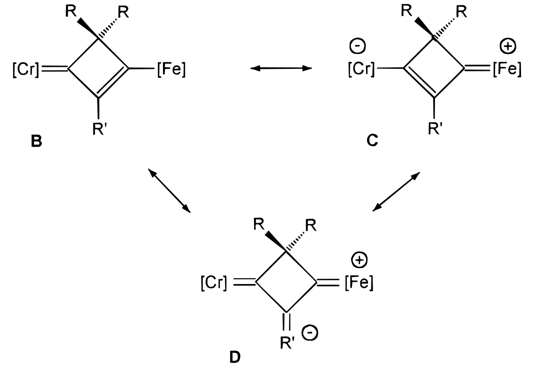
In the ^{1}H NMR spectra both Me groups in **5** give rise to only one singlet at room temperature as well as at low temperature (−80 °C). Therefore, rotation around the Fe−C bond and ring inversion is rapid on the NMR time scale (see below).

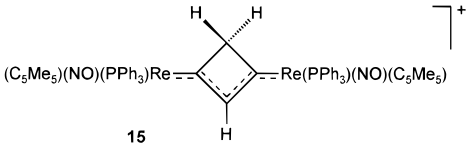
The ^{13}C resonances of both the chromium- (C-1) and iron-bound (C-3) ring carbon atoms appear at low field. The signals of the C-1 atom in the aryl- and carbomethoxy-substituted complexes **5c**−**e** and **12** are in the region characteristic for alkoxycarbene complexes (δ 290−320). The C-1 resonances in the alkyl-substituted complexes (δ 217.6 (**11**) to 254.1 (**5b**)) lie in the range usually observed for aminocarbene complexes. However, they are at a significantly higher field than those of 3-amino-substituted cyclobutenylidene complexes such as **13** (δ 286.3). The resonances of the C-3 atoms are in the region characteristic for alkenyliron complexes. Increasing the donor ability of the substituent at C-2 causes a considerable high-field shift of both the C-1 and the C-3 resonances. However, the influence on C-1 is more pronounced than that on C-3. Increasing the back-bonding properties of the [FeCO(L)Cp] fragment by variation of L (CO, P(OMe)$_3$, PPh$_3$) causes a slight upfield shift of the C-3, a downfield shift of the C-2, and an upfield shift of the C-1 resonances. Again, the C-1 signal is the most strongly affected. Surprisingly, the C-1 and C-3 resonances are also considerably influenced by the substituents at the sp^3 ring atom C-4. These spectroscopic results indicate that for a description of the overall bonding situation in these heterobinuclear cyclobutenylidene complexes several resonance structures have to be taken into account (Scheme 3).

Scheme 3



Molecular Structures of 5e, 10 and 11. The structures of the complexes **5e**, **10**, and **11** were additionally established by X-ray structural analyses (Tables 1 and 2). All compounds show structural peculiarities. The structure of **5e** dimethyl-substituted at C-4 (Figure 1), on the one hand, and those of the spirocyclic complexes **10** (Figures 2 and 3) and **11** (Figure 4), on the other hand, differ slightly; the core structures of **10** and **11**, however, are identical within error limits. Obviously, the structural consequences of substitution of P(OMe)$_3$ for CO are negligible.

Until now, only two homobinuclear cyclobutenylidene complexes (**15**[13] and **16**[24]) have been characterized by X-ray crystallography. The structures of two cyclobut-1-en-3-one iron complexes (complex **14**[25] and its dppe derivative[26]) have also been determined as well as those of a 3-diethylamino-substituted (**17**)[4] and a 3-ethoxy-substituted pentacarbonyl(cyclobutenylidene)tungsten complex (**18**).[4]



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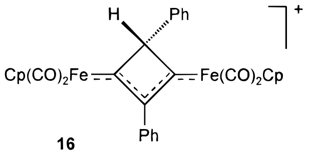
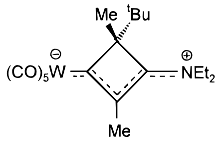


16



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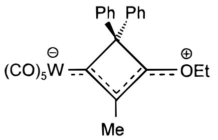

18

In these complexes the four-membered ring is nearly planar. The angle between the planes formed by the atoms C(7), C(6), C(9) and C(7), C(8), C(9) (for the numbering scheme, see Figure 1) ranges from 172.7° (in **14**)[25] to 179.5° (in [Cp(dppe)Fe$\overline{\mathrm{C{=}CMeC({=}O)C}}Ph_2$]).[26] Free cyclobut-1-en-3-ones are also almost planar. The

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[24] Slovokhotov, Yu. L.; Yanovskyi, A. I.; Andrianov, V. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1980**, *184*, C57.

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Table 2. Crystallographic Data for 5e, 10, and 11

	5e	10	11
empirical formula	$C_{20}H_{14}CrFeO_9$	$C_{25}H_{24}CrFeO_7$	$C_{27}H_{33}CrFeO_9P$
fw	506.2	544.3	640.4
cryst size, mm^3	0.35 × 0.35 × 0.35	0.5 × 0.5 × 0.5	0.3 × 0.3 × 0.3
cryst system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a, Å	11.011(2)	9.380(3)	9.824(4)
b, Å	11.479(3)	14.912(4)	12.743(4)
c, Å	16.509(4)	18.153(4)	13.135(5)
α, deg			93.08(3)
β, deg	96.61(2)	93.44(2)	108.44(3)
γ, deg			106.87(3)
V, Å^3	2072.7(9)	2534.5(11)	1473.4(9)
Z	4	4	2
d_{calcd}, g cm^{-3}	1.622	1.426	1.443
temp, K	243	250	233
μ, mm^{-1}	1.259	1.029	0.952
no. of indep rflns	4525	5506	6450
no. of obsd rflns ($F > 4\sigma(F)$)	3415	4323	4887
no. of params refined	280	307	352
R	0.037	0.058	0.045
R_{w}	0.036	0.070	0.048
resid electron density, e Å^{-3}	0.34	1.12	0.70

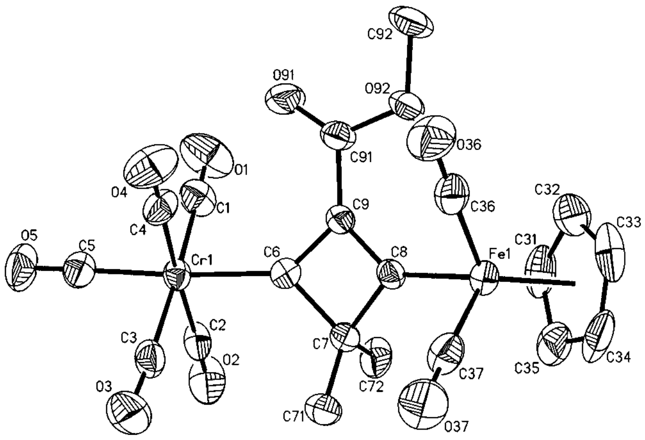

Figure 1. Structure of complex **5e** (hydrogen atoms omitted).

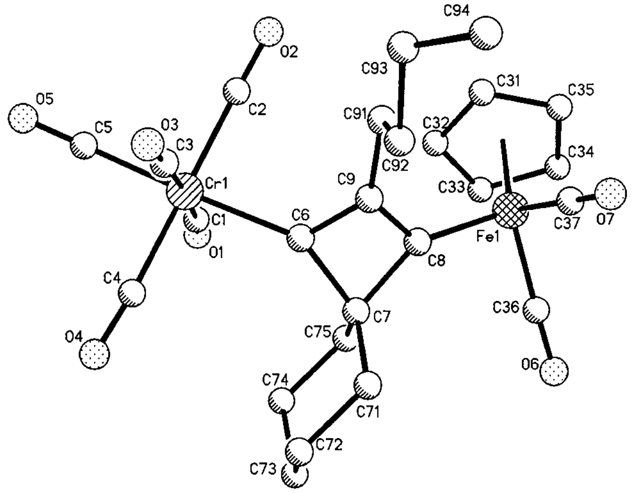

Figure 2. Structure of complex **10** (hydrogen atoms omitted).

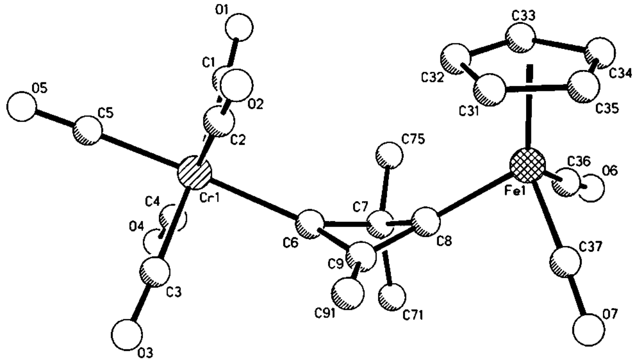

Figure 3. Partial view of complex **10** (hydrogen atoms and parts of ring substituents omitted).

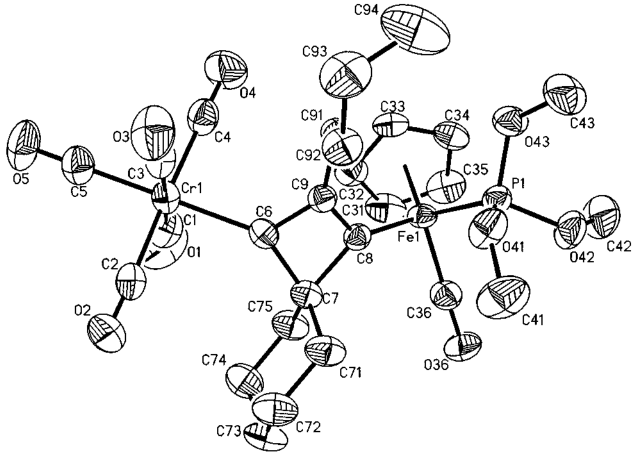

Figure 4. Structure of complex **11** (hydrogen atoms omitted).

puckering angle is 178.1° in $\mathrm{O{=}\overline{CCMe{=}C(OEt)C}Ph_2}$[27] and 177.7° in $\mathrm{O{=}\overline{CC[C(O)^tBu]{=}C(NHMe)C}(Tol)H}$.[28] In contrast to these compounds, the rings in **5e**, **10**, and **11** are strongly puckered. In **5e** the angle is 160.0°. In **10** (see Figure 3) and **11** the angle is even smaller: 143.9° (**10**) and 144.9° (**11**). As a consequence of the puckering the transannular distance C(6)−C(8) is small in **5e** (2.048(5) Å) and even smaller in **10** (1.929(5) Å) and **11** (1.930(5) Å). These distances are well below the sum of the van der Waals distances. Therefore, direct electronic interaction seems possible.

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(28) Hirokami, S.-I.; Takahashi, T.; Nagata, M.; Yamazaki, T. *J. Org. Chem.* **1987**, *52*, 2455.

Both C(sp^2)−C(sp^2) bond lengths are similar, C(6)−C(9) being slightly longer than C(8)−C(9). The difference in bond lengths increases in the series **11** → **10** → **5e**. 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).[29] The bond alternation is more pronounced in **18** (1.419(6) versus 1.387(7) Å)[4] and cyclobutenones and is reversed in **17** (1.371(8) versus 1.436(9) Å).[4]

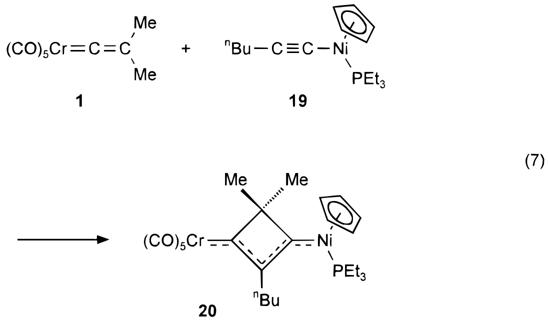
The Cr(1)−C(6) distance in **5e** (2.010(3) Å) is significantly shorter than the bond lengths in **10** (2.093(4) Å) and **11** (2.109(3) Å). This indicates a more pronounced π-back-donation from the [(CO)$_5$Cr] fragment into the ring in **5e**, probably due to the strong acceptor properties of the COOMe substituent at the 2-position. However, all distances are in the typical range of aminocarbene(pentacarbonyl) complexes.[30] As is usually observed with 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.

As expected, the Fe(1)−C(8) distances in the [Cp(CO)$_2$Fe] complexes **5e** and **10** are identical, whereas Fe(1)−C(8) in the (MeO)$_3$P-substituted complex **11** is slightly shorter. The distances are comparable to those in the cyclobut-1-en-3-one complex **14**[25] and its dppe derivative.[26]

The C(9)−C(91) distance in **5e** is short and compares well with the C−C single-bond distance in R$_2$C=CR−COOR.[29] The plane of the COOMe substituent at C-2 almost coincides with the "carbene" plane C(6), C(7), C(9) (torsion angle C(6)−C(9)−C(91)−O(91) = 2.7(5)°), indicating π-interaction between C=O and the ring (see the mesomeric structure **C** in Scheme 3).

The structural results of **5e**, **10**, and **11** confirm the conclusions from the spectroscopic data that the bonding situation in these heterobinuclear cyclobutenylidene complexes is best represented by the mesomeric structures **B**−**D** in Scheme 3, with **B** and **C** dominating. The relative importance of **B**−**D** can be influenced by the substituents at C-1, C-2, and C-3.

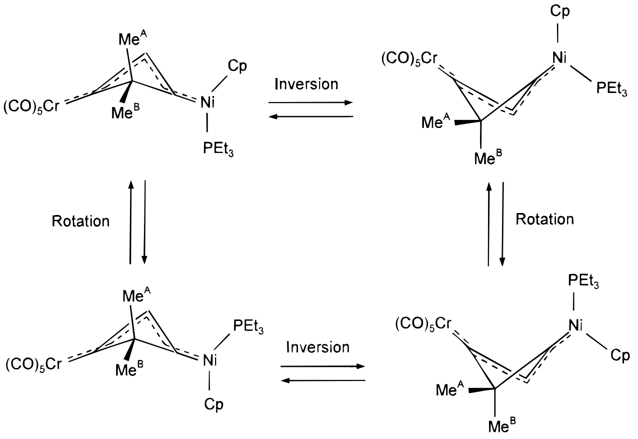
Reaction of 1 with [Cp(PEt$_3$)NiC≡C^{n}Bu]. Cycloaddition of alkynyl complexes to the C=C bond of vinylidenechromium complexes is not confined to iron alkynyl complexes. The reaction of **1** with, for example, [Cp(PEt$_3$)NiC≡C^{n}Bu] (**19**) gave, after chromatographic workup, the cyclobutenylidene complex **20** in 27% yield (eq 7).



(7)

Complex **20** exhibits fluxional behavior. Similar to the case for the complexes **5**, the ^{1}H NMR spectrum of **20** shows at room temperature only one singlet for the Me groups. However, below −40 °C two resonances of equal intensity (δ 1.28 and 1.32 in CD$_2$Cl$_2$ at 233 K) are observed. These signals coalesced at 275 K; $\Delta G^‡(T_c)$ was calculated to be 60.4 ± 0.5 kJ/mol.

Scheme 4



For electronic reasons the plane formed by P, Ni, and Cp(centroid) in **20** should be orthogonal to the C(7), C(8), C(9) plane. A related conformation has been observed for the alkenylnickel complex [Cp(PPh$_3$)NiC(−CPh=C{CN}$_2$)=C(CN)$_2$].[31] Therefore, there are four distinct conformations for **20** which interconvert either by ring inversion or by rotation about the Ni−C bond (Scheme 4).

Only rapid (on the NMR time scale) ring inversion *and* rotation render both Me groups equivalent. If both dynamic processes are slow, four resonances are to be expected. Therefore, one of the two dynamic processes is still fast at −40 °C. Since no broadening of the Me resonance is observed when solutions of **5** are cooled to −80 °C, the activation barrier $\Delta G^‡$ very likely applies to the rotation around the Ni−C bond.

Solvent Dependence of the UV/Vis Absorption. Within a group of related polar compounds the solvatochromic effect gives important hints on the relative extent of the second-order nonlinear optical properties.[32] As expected from the polar resonance structures **B** and **C**, all heterobinuclear cyclobutenylidene complexes exhibit a negative solvatochromic effect. The UV/vis absorption at lowest energy shifts toward 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 influenced by the different substituents at C-2, C-3, and C-4 of the ring. With increasing donor properties of the substituent at C-2, the solvent effect increases. The solvent shift $\Delta\tilde{\nu}$(pentane−DMF) of **5a**−**e** correlates well (correlation coefficient $r^2 = 0.91$) with the ^{13}C NMR resonances of C-2 (Figure 5).

There is no straightforward dependence of $\Delta\tilde{\nu}$ on the back-bonding abilities of the L$_n$M substituent at C-3, although within the Fe complex series **5a**, **7**, **9** increasing electron density at the metal tends to decrease the solvent effect: $\Delta\tilde{\nu}$(pentane−DMF) = 1240 (**5a**), 530 (**7**),

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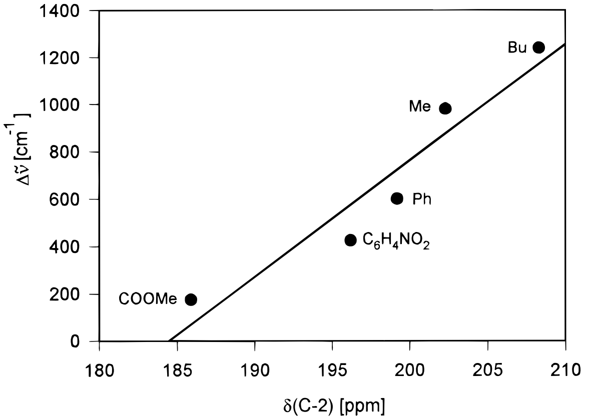

Figure 5. Correlation between ^{13}C NMR resonances of C-2 of **5a**−**e** and the solvatochromic effect $\Delta\tilde{\nu}$(pentane−DMF) in cm^{-1}.

670 cm^{-1} (**9**). When both Me substituents at C-4 are replaced by C_5H_{10} (**5a** → **10**), $\Delta\tilde{\nu}$(pentane−DMF) almost doubles ($\Delta\tilde{\nu} = 1240$ (**5a**), 2400 cm^{-1} (**10**)), presumably due to the reduction of the puckering angle of the ring and thus increased transannular interaction of C-1 and C-3.

Concluding Remarks

These results demonstrate that 1,3-heterobinuclear cyclobutenylidene complexes are readily available by [2 + 2] cycloaddition of alkynyl complexes to vinylidene complexes. In contrast to homobinuclear cyclobutenylidene complexes the ring in heterobinuclear cyclobutenylidene complexes adopt a “butterfly” conformation in the solid state. On the basis of the NMR spectra the complexes are fluxional in solution. These complexes are thermally stable. The spectroscopic data as well as the X-ray structural analyses of **5e**, **10**, and **11** indicate strong electronic communication between the metal centers. All 1,3-heterobinuclear cyclobutenylidene complexes exhibit a pronounced negative solvatochromic effect, the extent of which is influenced by the nature of the substituents at the “bridging” carbon atoms C-2 and C-4 of the C_4R_3 moiety. Investigations to determine the second-order nonlinear optical properties (NLO) of this class of compounds are presently in progress.

Experimental Section

General Comments. All operations were performed under an inert atmosphere (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 (Baker, silica gel for flash chromatography) was nitrogen-saturated. The yields refer to analytically pure compounds and were not optimized. Instrumentation: ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AC 250 or a Bruker WM 250 spectrometer; ^{31}P NMR spectra were recorded with a JEOL JNX 400 spectrometer. ^{1}H and ^{13}C NMR resonances are reported relative to TMS and ^{31}P NMR resonances relative to external H_3PO_4. Other instruments used are as follows: IR, Biorad FTS 60 spectrophotometer; MS, Finnigan MAT 312; UV/vis, Hewlett-Packard diode array spectrophotometer 8452A; elemental analyses, Heraeus CHN-O-RAPID.

The alkynyl complexes **4a**,[33] **4b**,[33] **4c**,[33] **4e**,[34] **6**,[18], **8**,[33] and **19**,[35] diphenylacetyl chloride,[36] and C_8K[37] were prepared according to literature procedures. Complex **4d** was prepared by following the procedure described in ref 34 for **4e**. Cyclohexanecarbonyl chloride and isobutyryl chloride were obtained from Aldrich Chemical Co. and Fluka, respectively.

Generation of the Vinylidene Complexes 1−3. At −80 °C 5.0 mmol (1.1 g) of $Cr(CO)_6$ was added to a suspension of 10.0 mmol of C_8K (1.34 g) in 50 mL of THF. The mixture was warmed to 0 °C, stirred for 1 h at that temperature, and then cooled to −80 °C. A 5 mmol amount of the acyl chloride was added. The mixture was again warmed to 0 °C and stirred for 30 min. The solvent was removed in vacuo at −20 °C, and the residue was suspended at −80 °C in 50 mL of CH_2Cl_2. A 5.0 mmol (0.7 mL) amount of trifluoroacetic anhydride was added and the mixture stirred for 30 min. The deep green suspension was transferred to the top of a frit filled with a 3 cm layer of silica and cooled to −60 °C. Elution with ca. 100 mL of CH_2Cl_2 and concentration of the eluate to a volume of ca. 30 mL gave deep green solutions of the vinylidene complexes. These vinylidene complexes are thermally very unstable. Therefore, they were only identified by their ν(CO) spectra and not isolated. The solutions were immediately used for the subsequent reactions.

Pentacarbonyl(dimethylvinylidene)chromium (1). IR (CH_2Cl_2): ν(CO) 2080 m, 1979 vs, 1960 sh cm^{-1}. ^{1}H NMR (CD_2Cl_2, 198 K): δ 1.83 (s, br, Me). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 198 K): δ 25.3 (Me), 172.7 (C_β), 216.3 (*cis*-CO), 223.8 (*trans*-CO), 365.8 (C_α).

Pentacarbonyl(pentamethylenevinylidene)chromium (2).[13] IR (CH_2Cl_2): ν(CO) 2082 s, 2011 sh, 1994 vs, 1973 vs cm^{-1}. ^{1}H NMR (CD_2Cl_2, 193 K): δ 1.54 (m, 6 H), 2.14 (m, 4 H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 193 K): δ 21.7, 25.1, 25.7 (CH_2), 121.3 (C_β), 213.1 (*cis*-CO), 225.9, (*trans*-CO), 399.3 (C_α).

Pentacarbonyl(diphenylvinylidene)chromium (3).[13] IR (CH_2Cl_2): ν(CO) 2088 s, 2027 sh, 2002 vs, 1977 vs cm^{-1}. ^{1}H NMR (CD_2Cl_2, 228 K): δ 7.15−7.45 (m, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 223 K): δ 127.1, 128.1, 129.0, 130.6 (Ph), 133.7 (C_β), 211.9 (*cis*-CO), 222.8 (*trans*-CO), 405.9 (C_α).

Preparation of the Complexes 5, 7, 9−12 and 20. At −60 °C a solution of 5.0 mmol of the alkynyl complexes in 50 mL of CH_2Cl_2 was added to a solution of the vinylidene complexes **1**−**3** in CH_2Cl_2. The mixture was stirred for 20 min at −60 °C and then for 30 min at room temperature. The solvent was removed in vacuo, and the residue was chromatographed on silica gel at −30 °C. The complexes were eluted with pentane/CH_2Cl_2 (ratio decreasing from 1/0 to 1/1) as orange or red solutions. The solvent was removed in vacuo, and the complexes were crystallized from 20 mL of pentane/CH_2Cl_2 as described below.

Pentacarbonyl[2-*n*-butyl-3-{dicarbonyl(η^5-cyclopentadienyl)ferrio}-4,4-dimethylcyclobut-2-en-1-ylidene]chromium (5a). Yield: 1.00 g (40% based on $Cr(CO)_6$) of yellow crystals from pentane/CH_2Cl_2 (1:1). Mp: 64 °C. IR (CH_2Cl_2): ν(CO) 2049 m, 2028 s, 1982 s, 1923 vs cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ 0.93 (t, $^{3}J_{HH} = 6.91$ Hz, 3H, Me), 1.41 (s, br, 10H, CH_2 and Me), 2.62 (t, $^{3}J_{HH} = 7.45$ Hz, 2H, CH_2), 4.93 (s, 5H, C_5H_5). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 298 K): δ 13.8 (Me), 22.7 (CH_2), 28.3 (Me), 28.6, 29.8 (CH_2), 76.0 (4-C), 86.0 (C_5H_5), 208.3 (2-C), 208.8 (3-C), 212.2 (Fe−CO), 218.9 (*cis*-CO), 225.9 (*trans*-CO), 242.6 (1-C). UV/vis (λ_{max}, nm (log ϵ)): 452 (3.974) [pentane]; 428 (3.901) [DMF]. Anal. Calcd for $C_{22}H_{20}CrFeO_7$ (504.2): C, 52.40; H, 4.00. Found: C, 52.49; H, 3.87.

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[37] (a) *Handbuch der Präparativen Anorganischen Chemie*; Brauer, G., Ed.; Ferdinand Enke Verlag: Stuttgart, Germany, 1978; Vol. 2. (b) Savoia, D.; Trombini, C.; Umani-Ronchi, A. *Pure Appl. Chem.* **1985**, *57*, 1887.

Pentacarbonyl[3-{dicarbonyl(η^5-cyclopentadienyl)ferrio}-2,4,4-trimethylcyclobut-2-en-1-ylidene]chromium (5b). Yield: 0.67 g (29% based on $Cr(CO)_6$) of red crystals from pentane/CH_2Cl_2 (7:3). Mp: 88 °C. IR (CH_2Cl_2): ν(CO) 2049 m, 2029 s, 1984 s, 1923 vs cm^{-1}. ^{1}H NMR (CD_2Cl_2, 273 K): δ 1.37 (s, 6H, Me), 2.22 (s, 3H, Me), 4.98 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR (CD_2Cl_2, 223 K): δ 14.6, 27.6 (Me), 75.4 (4-C), 85.8 (C_5H_5), 202.3 (2-C), 212.0 (3-C), 216.1 (Fe−CO), 218.6 (*cis*-CO), 226.3 (*trans*-CO), 254.1 (1-C). UV/vis (λ_{max}, nm (log ϵ)): 462 (4.051) [pentane]; 442 (3.987) [DMF]. MS (70 eV; *m/z* (%)): 462 (35) [M$^+$], 434 (8) [(M − CO)$^+$], 406 (19) [(M − 2CO)$^+$], 378 (7) [(M − 3CO)$^+$], 350 (48) [(M − 4CO)$^+$], 322 (66) [(M − 5CO)$^+$], 294 (28) [(M − 6CO)$^+$], 266 (100) [(M − 7CO)$^+$]. Anal. Calcd for $C_{19}H_{14}CrFeO_7$ (462.12): C, 49.36; H, 3.05. Found: C, 49.26; H, 3.10.

Pentacarbonyl[3-{dicarbonyl(η^5-cyclopentadienyl)ferrio}-4,4-dimethyl-2-phenyl-2-cyclobut-2-en-1-ylidene]chromium (5c). Yield: 0.92 g (35% based on $Cr(CO)_6$) of dark red crystals from pentane/CH_2Cl_2 (3:1). Mp: 82 °C. IR (pentane): ν(CO) 2051 m, 2028 s, 1986 m, 1948 vs, 1933 s cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ 1.46 (s, 6H, Me), 4.83 (s, 5H, C_5H_5), 7.33−7.45 (m, 5H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 26.6 (Me), 76.5 (4-C), 86.0 (C_5H_5), 128.3, 128.5, 130.7, 136.9 (Ph), 199.2 (2-C), 211.9 (Fe−CO), 217.9 (*cis*-CO), 228.3 (*trans*-CO), 241.2 (3-C), 304.9 (1-C). UV/vis (λ_{max}, nm (log ϵ)): 490 (4.148) [pentane]; 476 (4.159) [DMF]. Anal. Calcd for $C_{24}H_{16}CrFeO_7$ (524.23): C, 54.99; H, 3.08. Found: C, 54.59; H, 3.22.

Pentacarbonyl[3-{dicarbonyl(η^5-cyclopentadienyl)ferrio}-2-(*p*-nitrophenyl)-4,4-dimethylcyclobut-2-en-1-ylidene]chromium (5d). Yield: 1.14 g (40% based on $Cr(CO)_6$) of dark red crystals from pentane/CH_2Cl_2 (3:2). Mp: 85 °C dec. IR (CH_2Cl_2): ν(CO) 2051 s, 2030 s, 1988 m, 1936 vs, 1925 sh cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ 1.46 (s, 6H, Me), 4.90 (s, 5H, C_5H_5), 7.53 and 7.57 (m, 2H, C_6H_4), 8.31 and 8.34 (m, 2H, C_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 26.4 (Me), 72.6 (4-C), 86.0 (C_5H_5), 123.8, 129.8, 144.3, 147.7 (C_6H_4), 196.2 (2-C), 211.5 (Fe−CO), 217.4 (*cis*-CO), 227.9 (*trans*-CO), 244.3 (3-C), 312.6 (1-C). UV/vis (λ_{max}, nm (log ϵ)): 490 (4.087) [pentane]; 480 (4.176) [DMF]. Anal. Calcd for $C_{24}H_{15}CrFeNO_9$ (569.0): C, 50.62; H, 2.66; N, 2.46. Found: C, 50.64; H, 2.80; N, 2.71.

Pentacarbonyl[2-(carbomethoxy)-3-{dicarbonyl(η^5-cyclopentadienyl)ferrio}-4,4-dimethylcyclobut-2-en-1-ylidene]chromium (5e). Yield: 0.76 g (30% based on $Cr(CO)_6$) of brown crystals from pentane/CH_2Cl_2 (2:3). Mp: 76 °C. IR (CH_2Cl_2): ν(CO) 2056 m, 2035 s, 1981 s, 1941 vs, 1936 sh, 1751 m cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ 1.41 (s, 6H, Me), 3.89 (s, 3H, OMe), 5.07 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 26.5 (Me), 50.8 (OMe), 74.7 (4-C), 86.7 (C_5H_5), 163.7 (*C*OOMe), 185.9 (2-C), 211.0 (Fe−CO), 217.6 (*cis*-CO), 228.6 (*trans*-CO), 257.0 (3-C), 314.8 (1-C). UV/vis (λ_{max}, nm (log ϵ)): 482 (4.101) [pentane]; 478 (4.181) [DMF]. Anal. Calcd for $C_{20}H_{14}CrFeO_9$ (506.2): C, 47.46; H, 2.79. Found: C, 47.83; H, 2.98.

Pentacarbonyl[2-*n*-butyl{carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)ferrio}-4,4-dimethylcyclobut-2-en-1-ylidene]chromium (7). Yield: 1.38 g (46% based on $Cr(CO)_6$) of orange crystals from pentane/CH_2Cl_2 (2:3). Mp: 83 °C. IR (CH_2Cl_2): ν(CO) 2041 m, 1952 s, 1916 vs cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ 0.93 (t, $^3J_{HH}$ = 6.3 Hz, 3H, Me), 1.31 (s, 3H, Me), 1.37−1.48 (m, br, 4H, 4 × CH_2), 1.48 (s, 3H, Me), 2.59−2.64 (m, br, 2H, CH_2), 3.64 (d, $^3J_{PH}$ = 11.3 Hz, 9H, OMe), 4.70 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 14.0 (Me), 23.1 (CH_2), 25.9, 29.1 (Me), 29.9, 32.1 (CH_2), 52.8 (d, $^3J_{CP}$ = 7.2 Hz, OMe), 76.3 (4-C), 84.2 (C_5H_5), 208.7 (2-C), 216.5 (d, $^2J_{CP}$ = 45.9 Hz, Fe−CO), 219.9 (*cis*-CO), 225.1 (d, $^2J_{CP}$ = 33.3 Hz, 3-C), 225.9 (*trans*-CO), 234.5 (1-C). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 179.3 (s). UV/vis (λ_{max}, nm (log ϵ)): 440 (3.989) [pentane]; 430 (3.938) [DMF]. Anal. Calcd for $C_{24}H_{29}CrFeO_9P$ (600.26): C, 48.02; H, 4.87. Found: C, 47.70; H, 4.85.

Pentacarbonyl[2-*n*-butyl-3-{carbonyl(η^5-cyclopentadienyl)(triphenylphosphine)ferrio}-4,4-dimethylcyclobut-2-en-1-ylidene]chromium (9). Yield: 0.74 g (20% based on $Cr(CO)_6$) of orange crystals from pentane/CH_2Cl_2 (3:2). Mp: 148 °C. IR (CH_2Cl_2): ν(CO) 2042 m, 1948 m, 1919 vs cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ 0.76 (t, $^3J_{HH}$ = 7.0 Hz, 3H, Me), 1.02−1.35 (m, br, 10H, 4 × CH_2 and 2 × Me), 2.15−2.26 (m, br, 1H, CH_2), 2.49−2.56 (m, br, 1H, CH_2), 4.56 (d, J_{PH} = 1.29 Hz, 5H, C_5H_5), 7.21−7.52 (m, br, 15H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 13.9 (Me), 22.3 (CH_2), 22.9 (Me), 29.7, 34.1 (CH_2), 78.4 (4-C), 85.2 (C_5H_5), 128.5, 128.7, 130.6, 133.0, 133.1, 135.0, 135.7 (Ph), 210.2 (2-C), 218.8 (d, $^2J_{CP}$ = 30.8 Hz, Fe-CO), 219.9 (*cis*-CO), 224.9 (d, $^2J_{CP}$ = 16.8 Hz, 3-C), 225.3 (*trans*-CO), 227.9 (1-C). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 70.8 (s). UV/vis (λ_{max}, nm (log ϵ)): 428 (3.967) [pentane]; 416 (3.928) [DMF]. Anal. Calcd for $C_{39}H_{35}CrFeO_6P$ (738.49): C, 63.43; H, 4.78. Found: C, 63.71; H, 5.30.

Pentacarbonyl[2-*n*-butyl-3-{dicarbonyl(η^5-cyclopentadienyl)ferrio}-spiro[5.3]non-2-en-1-ylidene]chromium (10). Yield: 0.82 g (30% based on $Cr(CO)_6$) of orange crystals from pentane/CH_2Cl_2 (1:1). Mp: 74 °C. IR (pentane): ν(CO) 2047 m, 2027 m, 1980 m, 1920 vs cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ 0.92 (t, br, 3H, Me), 1.34−1.93 (m, 14H, 7 × CH_2), 2.75 (t, br, 2H, CH_2), 4.88 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 13.8 (Me), 22.8, 24.1, 25.5, 29.5, 29.9, 39.8, (CH_2), 82.1 (4-C), 85.9 (C_5H_5), 190.5 (2-C), 212.4 (Fe−CO), 214.1 (3-C), 219.1 (*cis*-CO), 224.0 (*trans*-CO), 224.2 (1-C). UV/vis (λ_{max}, nm (log ϵ)): 440 (3.834) [pentane]; 398 (3.888) [DMF]. Anal. Calcd for $C_{25}H_{24}CrFeO_7$ (544.3): C, 55.17; H, 4.44. Found: C, 55.14; H, 4.43.

Pentacarbonyl[2-*n*-butyl-3-{carbonyl(η^5-cyclopentadienyl)(trimethyl phosphite)ferrio}spiro[5.3]non-2-en-1-ylidene]chromium (11). Yield: 1.18 g (37% based on $Cr(CO)_6$) of orange crystals from pentane/CH_2Cl_2 (2:3). Mp: 140 °C. IR (CH_2Cl_2): ν(CO) 2042 m, 1947 m, 1916 vs, 1889 sh cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ 0.92 (t, $^3J_{HH}$ = 7.1 Hz, 3H, Me), 1.26−2.00 (m, 14H, CH_2), 2.73 (t, br, 2H, CH_2), 3.62 (d, $^3J_{PH}$ = 11.2 Hz, 9H, OMe), 4.61 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 14.1 (Me), 23.2, 23.7, 24.6, 25.8, 29.6, 29.7, 36.2, 43.6 (CH_2), 52.7 (d, $^3J_{CP}$ = 7.5 Hz, OMe), 81.6 (4-C), 83.9 (C_5H_5), 205.0 (d, $^3J_{CP}$ = 31.2 Hz, 2-C), 213.7 (d, $^2J_{CP}$ = 5.4 Hz, 3-C), 217.0 (d, $^2J_{CP}$ = 47.1 Hz, Fe−CO), 217.6 (1-C), 219.8 (*cis*-CO), 224.5 (*trans*-CO). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 180.8 (s). UV/vis (λ_{max}, nm (log ϵ)): 416 (3.457) [pentane]; 392 (3.875) [DMF]. Anal. Calcd for $C_{27}H_{33}CrFeO_9P$ (640.3): C, 50.64; H, 5.19. Found: C, 50.61; H, 5.21.

Pentacarbonyl[2-*n*-butyl-3-{dicarbonyl(η^5-cyclopentadienyl)ferrio}-4,4-diphenylcyclobut-2-en-1-ylidene]chromium (12). Yield: 0.47 g (15% based on $Cr(CO)_6$) of black crystals from pentane/CH_2Cl_2 (3:2). Mp: 170 °C dec. IR (pentane): ν(CO) 2050 m, 2030 m, 1989 m, 1945 vs, 1931 sh cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ 0.94 (t, $^3J_{HH}$ = 7.2 Hz, 3H, Me), 1.37−1.61 (m, 4H, CH_2), 2.58−2.64 (m, 2H, CH_2), 4.58 (s, 5H, C_5H_5), 7.26−7.42 (m, 10H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 13.7 (Me), 22.9, 29.7, 30.3 (CH_2), 84.3 (4-C), 86.3 (C_5H_5), 126.9, 128.0, 130.1, 142.9 (Ph), 203.0 (2-C), 212.1 (Fe−CO), 217.5 (*cis*-CO), 227.1 (*trans*-CO), 231.8 (3-C), 296.0 (1-C). UV/vis (λ_{max}, nm (log ϵ)): 504 (3.915) [pentane]; 484 (3.856) [DMF]. Anal. Calcd for $C_{32}H_{24}CrFeO_7$ (628.34): C, 61.17; H, 3.85. Found: C, 61.12; H, 4.26.

Pentacarbonyl[2-*n*-butyl-3-{η^5-cyclopentadienyl(triethylphosphine)nickelio}-4,4-dimethylcyclobut-2-en-1-ylidene]chromium (20). Yield: 0.77 g (27% based on $Cr(CO)_6$) of brown crystals from pentane/CH_2Cl_2 (1:1). Mp: 65 °C. IR (pentane): ν(CO) 2044 m, 1923 vs cm^{-1}. ^{1}H NMR (CD_2Cl_2, 233 K): δ 0.89 (t, $^3J_{HH}$ = 6.9 Hz, 3H, Me), 0.99−1.11 (m, 9H, CH_2CH_3), 1.28 (s, 3H, Me), 1.32 (s, 3H, Me), 1.35−1.49 (m, 10H, 2 × CH_2 and 3 × PCH_2), 2.56−2.64 (m, 2H, CH_2), 5.23 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR (CD_2Cl_2, 233 K): δ 7.6 (CH_2CH_3), 13.9 (Me), 18.3 (d, $^2J_{PH}$ = 28.5 Hz, PCH_2), 22.7 (CH_2), 28.2 (Me), 29.5 (CH_2), 29.6 (Me), 30.4 (CH_2), 74.8 (4-C), 90.9 (C_5H_5), 204.5 (d, $^3J_{CP}$ = 23.9 Hz, 2-C), 208.6 (3-C), 219.3

(*cis*-CO), 224.1 (*trans*-CO), 225.6 (1-C). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 31.2 (s). UV/vis (λ_{max}, nm (log ϵ)): 448 (2.031) [pentane]; 420 (3.929) [DMF]. MS (FAB, 2-nitrophenyl octyl ether; *m/z* (%)): 568 (12) [M^+], 540 (4) [$(M - CO)^+$], 512 (10) [$(M - 2CO)^+$], 456 (32) [$(M - 4CO)^+$], 450 (100) [$(M - PEt_3)^+$], 428 (24) [$(M - 5CO)^+$], 422 (48) [$(M - PEt_3 - CO)^+$], 394 (26) [$(M - PEt_3 - 2CO)^+$], 376 (60) [$(M - Cr(CO)_5)^+$], 366 (18) [$(M - PEt_3 - 3CO)^+$], 338 (22) [$(M - PEt_3 - 4CO)^+$]. Anal. Calcd for $C_{26}H_{35}CrNiO_5P$ (568.1): C, 54.92; H, 6.21. Found: C, 55.13; H, 6.31.

X-ray Structural Analyses of 5e, 10, and 11. Single crystals were grown from pentane/CH_2Cl_2 (2:3 (**5e**), 1:1 (**10**), 2:3 (**11**)) and mounted in a glass capillary. All crystal data were collected on a Siemens R3m/V diffractometer (Wyckoff scan, $4° < 2\theta < 54°$) with a graphite monochromator (Mo Kα, $\lambda = 0.710\,73$ Å). Semiempirical absorption corrections were carried out (ψ scans with 10 reflections). The structures were solved with Patterson methods and refined by full-matrix least-squares techniques (Siemens SHELXTL PLUS).

The butyl group of **10** is disordered. This leads to high thermal parameters for C(93) and C(94). Many efforts to model the disorder by varying the occupancy factors and atom sites did not result in reasonable bond angles and lengths and did not lead to lower thermal parameters or *R* values. In the present model, the ultimate refinement was performed with bond length restraints for C(92)−C(93) and C(93)−C(94), resulting in reasonable bond angles. Similar problems occurred for C(72), C(73), and C(74) of the cyclohexane ring, but in this case no restraint was applied.

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Supporting Information Available: Tables of crystal data and refinement details, complete positional and thermal parameters, bond distances, bond angles, and torsion angles for compounds **5e**, **10**, and **11** and figures giving additional views of **10** (42 pages). Ordering information is given on any current masthead page.

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