(η^6-Arene)tricarbonylchromium and Ferrocene Complexes Linked to Binaphthyl Derivatives

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Palladium-catalyzed coupling reactions of 6,6′-dihydroxyboron-2,2′-dimethoxy-1,1′-binaphthyl **5g** and chloroarenetricarbonylchromium complexes **6a**−**c** afforded complexes **7a**−**c** with the binaphthyl residue directly linked to the (η^6-arene)tricarbonylchromium entity. Coupling reactions of 2,2′-dimethoxy, 3,3′-diodo, and 6,6′-diodo-1,1′-binaphthyl **3h** and **5h** with ethynylarenetricarbonylchromium derivatives **6d**−**f** and ethynylferrocene **9** yielded binaphthyl compounds linked to arenetricarbonylchromium and ferrocenyl derivatives **8a**−**c**, **11a**−**c**, **10**, and **12** through a triple bond. Condensation of 2,2′-dimethylmethoxy, 3-formyl, 1,1′-binaphthyl **2a** with (η^6-phenyl)methyltriphenylphosphonium tricarbonylchromium **13** and ferrocenylmethyltriphenylphosphonium **18** gave binaphthyl compounds linked to arenetricarbonylchromium and ferrocenyl derivatives **14** and **19**, respectively, through a double bond. X-ray analyses of the dinuclear chromium complex **8a** and of the mononuclear chromium complex **17-Z** are described.

Introduction

Carbon-bridged bimetallic π-conjugated complexes have attracted considerable interest due to their physical and chemical properties leading to potential application as a material with nonlinear optical properties.[1] In our laboratory, we have prepared such complexes by creating C−C bonds via different methodologies associating organic derivatives and η^5- and η^6-organometallic complexes.[2] Being involved in organometallic complexes and recently in 2,2′-dimethoxy-1,1′-binaphthyl compounds,[3] we combined the two experiences to prepare binapthyl derivatives associated with arenetricarbonylchromium and ferrocene complexes.[4,5c] Our final goal was to associate chiral *ortho* or *meta* disubstituted-arenetricarbonylchromium complexes with helicoïdal binaphthyl residues and to know if the combination of the planar and helicoïdal chiralities could enhance NLO activities. To our knowledge, only a few examples of binaphthyl derivatives substituted by organometallic complexes have been described in the literature. One implied cationic diiron complexes obtained by condensation of *ortho* monoaldehyde **1a** and dialdehyde **3a** and the cationic dinuclear complex $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{-}CH_3)]^+[BF_4]^-$,[5a] another one concerned the benzannulation of axial chiral biscarbene complexes of Cr,[5b] and a third one involved the combination of planar chirality and axial chirality by reaction of (*S*)-2-amino-2′-methoxy-1,1′-binaphthyl with the (*S*)- or (*R*)-ferrocenylpropenal. Here, we report efficient syntheses of (η^6-arene)tricarbonylchromium and ferrocene complexes linked to 2,2′-dialkoxy-1,1′-binaphthyl derivatives either directly or through different spacers such as a triple or a double bond.

Results and Discussion

The general strategy for the preparation of arenetricarbonylchromium or ferrocene derivatives linked to binaphthyl compounds was based on palladium-catalyzed coupling reactions such as Stille, Negishi, or Sonogashira reactions. Thus, we

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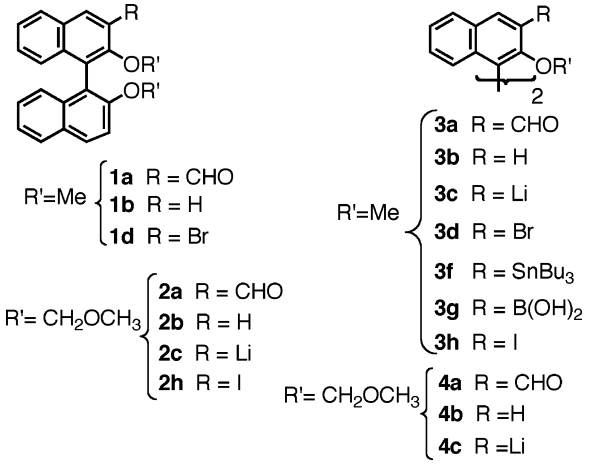
Scheme 1. Binaphthyl Derivatives 1, 2, and 3

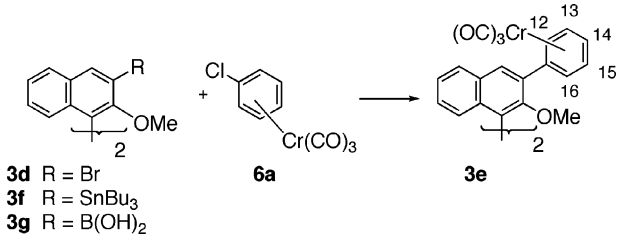


synthesized three series of compounds depending on the nature of the link between the binaphthyl residue and the organometallic entity: complexes **3e**, **7a**−**c** where the binaphthyl is directly linked to the arenetricarbonylchromium derivatives, complexes **8a**−**d**, **10**, **11a**−**c**, and **12** in which the spacer is a triple bond, and complexes **14**−**17** and **19** in which the spacer is a double bond.

Synthesis of the Starting Binaphthyl Derivatives. Racemic 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) treated with NaH and MeI yielded the dimethoxy compound **3b**.[6] *ortho*-Lithiation of the diether gave the 2,2′-dilithio compound **3c**,[3c] which was trapped with DMF, Br_2, I_2, $ClSnBu_3$, and $B(OEt)_3$ to yield the dialdehyde **3a**[7] (71% yield), the dibromo **3d** (30% yield), the diodo **3h** (33% yield), the stannous derivative **3f** (38% yield), and the diboronic acid **3g** (37% yield), Scheme 1. Depending on the experimental conditions, the monoaldehyde **1a** and the monobromo derivative **1d** have been also recovered as byproducts. We prepared compound **2b**, which appeared to be more soluble in organic solvents in contrast to **1b**, by protecting the hydroxy groups of BINOL with a methyl methoxy group (MOM).[8] The choice of the protected methoxy methyl ether MOM group was dictated not only by a solubility problem, but also by the monolithiation/formylation sequence. Indeed, lithiation of **1b** required 3 equiv of *n*-BuLi, whereas lithiation of **2b** occurred with only 1 equiv of *n*-BuLi. DMF trapping gave the monoaldehyde **2a** in 60% yield together with the dialdehyde **4a** in 22% yield. Thus, **2b** was lithiated with *n*-BuLi into **2c** and trapped with I_2, giving the monoiodo compound **2h** in 49% yield.

Direct Link between the Binaphthyl Derivatives and the Arenetricarbonylchromium Complexes: Synthesis of 3e, 7a−**c.** We were first interested to test the addition of an organometallic moiety at the 3 or at the 3,3′ positions of the binaphthyl framework. Stille arylation of the bromo derivative **3d** and tributyltinbenzenetricarbonylchromium[9] failed to afford

Scheme 2. Synthesis of the Dinuclear Complex 3e



complex **3e** efficiently. Alternatively, condensation of the tin derivative **3f**[9] and bromobenzenetricarbonylchromium[10] was undertaken, but it was revealed to be also unsuccessful. Suzuki arylation of chlorobenzenetricarbonylchromium **6a**[10] with the boronic acid **3g** in the presence of $Pd(PPh_3)_4$ and $Ba(OH)_2$ as a base gave a mixture of compounds, but the expected complex **3e** was obtained as a minor product, Scheme 2. If K_2CO_3 was used as a base and if the reaction mixture was performed in acetone, complex **3e** was obtained in only 28% yield and was shown to be very unstable. We tried also to perform *ipso* nucleophilic aromatic substitution S_NAr[11] with fluorobenzenetricarbonylchromium[12] and the bis(naphthyllithium) derivative **3c**. Unfortunately, we recovered the starting material probably because the protons *ortho* to the fluoro group were too acidic and likely lithiated by **3c** and then hydrolyzed.

In view of these results, we investigated what could be the influence of steric hindrance of the boronic derivative on the course of the reaction by performing the reaction on a less hindered carbon. Consequently, we repeated an analogous experiment starting from the less crowded boronic acid at the C6 carbon **5g**. Thus, in the presence of $Pd(PPh_3)_4$, Na_2CO_3, and chloroderivatives **6a**−**c**,[13e] we successfully obtained the corresponding binaphthyl derivatives **7a**−**c** directly substituted by (η^6-arene)$Cr(CO)_3$ entities in 71%, 72%, and 74% yield, respectively, Scheme 3. A well-resolved ^1H NMR spectrum of the *ortho* derivative **7b** was obtained. Indeed, the four protons H_{13}, H_{14}, H_{15}, and H_{16} of the η^6 complex resonate at 5.18, 5.50, 5.18, and 5.62 ppm, respectively, in agreement with a major conformation of the $Cr(CO)_3$ tripod[13] in solution eclipsing the C_{12} carbon bearing the methyl group and the C_{14} and C_{16} carbons. The differences of chemical shift $\delta(H_{14}) - \delta(H_{13}) = 0.32$ and $\delta(H_{16}) - \delta(H_{15}) = 0.44$ ppm are noticeable, Table 1. No conclusion can be drawn for the major conformation of the tripod $Cr(CO)_3$ in solution for complexes **7a** and **7c**. For the naphthyl part, the five aromatic protons H_3, H_4, H_6, H_8, and H_9 resonate almost at the same frequencies for complexes **7a** and

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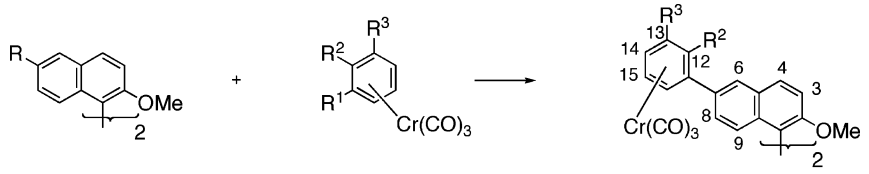
Scheme 3. Synthesis of the Dinuclear Complexes 7

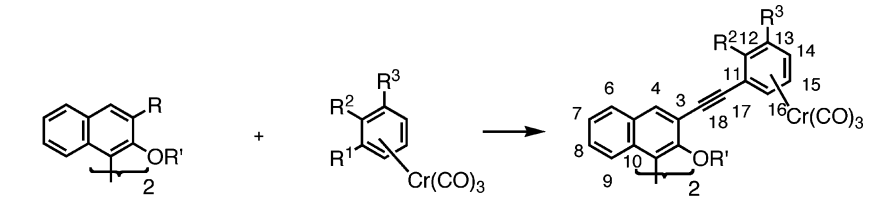


5g R = $B(OH)_2$

6a R^1 = Cl R^2 = R^3 = H
6b R^1 = Cl R^2 = Me R^3 = H
6c R^1 = Cl R^2 = H R^3 = Me

7a R^2 = R^3 = H
7b R^2 = Me R^3 = H
7c R^2 = H R^3 = Me

Scheme 4. Synthesis of the Dinuclear Complexes 8



R'=Me
3d R = Br
3h R = I
3i R = C≡CSiMe_3
3j R = C≡CH
R' = CH_2OCH_3
4h R = I

6a R^1 = Cl R^2 = R^3 = H
6d R^1 = C≡CH R^2 = R^3 = H
6e R^1 = C≡CH R^2 = Me R^3 = H
6f R^1 = C≡CH R^2 = H R^3 = Me

R'=Me
8a R^2 = R^3 = H
8b R^2 = Me R^3 = H
8c R^2 = H R^3 = Me
R' = CH_2OCH_3
8d R^2 = R^3 = H

Table 1. Selected ^{1}H NMR Data of Complexes 7a−c

complex	H_{12}	H_{13}	H_{14}	H_{15}	H_{16}
7a	5.77	5.49	5.34	5.49	5.77
7b		5.18	5.50	5.18	5.62
7c	5.17		5.58	5.58	5.58

complex	H_3	H_4	H_6	H_8	H_9
7a	7.49	8.02	8.01	7.32	7.13
7b	7.51	8.02	7.88	7.23	7.12
7c	7.49	8.02	8.01	7.33	7.13

7c; however, the two protons H_6 and H_8 of complex **7b** are unexpectedly shielded, Table 1. According to these results, we can assume that it is likely that the C3 and C3′ positions of the binaphthyl moiety were not reactive for a direct substitution by an arenetricarbonylchromium complex for steric reasons. Thus, we tried to link these two parts through a spacer, a triple or a double bond. The corresponding results are summarized next.

Binaphthyl Derivatives Linked to Arenetricarbonylchromium and Ferrocene Complexes through a Triple Bond: Synthesis of 8a−d, 10, 11a−c, and 12. Our first trial concerned the introduction of a triple bond between the naphthyl ring and the organometallic part by condensing the dibromo compound **3d** and ethynylarenetricarbonyl chromium **6d**[2c,d] using $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF or $Pd_2(dba)_3$, $AsPh_3$, Et_3N, THF at 40 °C, but this did not yield the expected chromium complex **8a**, Scheme 4. Repeating these condensations with the diiodo compounds **3h** and the alkyne **6d**, we obtained complex **8a** in 55% yield with $PdCl_2$ $(PPh_3)_2$, CuI, Et_3N, and THF and in 74% yield with Pd_2dba_3, $AsPh_3$ without CuI. This reaction has been generalized with *ortho* and *meta* ethynyltoluenetricarbonylchromium complexes **6e** and **6f**, which lead to the formation of the di-substituted complexes **8b** and **8c** in 60% and 90% yield, respectively, as diastereoisomer mixtures, Scheme 4.

Alternatively, complex **8a** was also obtained by condensing 3,3′-diethynyl-binaphthyl compound **3j** with chlorobenzenetricarbonylchromium complex **6a**. For this purpose, we reacted the diodo compound **3h** with trimethysilylacetylene, which afforded the trimethylsilylethynyl compound **3i** in 62% yield in the presence of $PdCl_2(PPh_3)_2$, CuI, and Et_3N. Cleavage of the C−Si bond with NaOH, 2 N in MeOH occurred almost in quantitative yield giving complex **3j**.[2a,10b] Next, coupling reaction using $Pd_2(dba)_3$, $AsPh_3$, Et_3N with chlorobenzenetricarbonylchromium **6a** and **3j** in THF (reflux 5h) yielded complex **8a** in 49% yield, Scheme 4. The reaction with the organometallic entity bearing the triple bond is slightly more efficient than the one involving the binaphthyl residue substituted by the triple bond. The yield of the coupling reaction was improved by using the diiodo derivative **4h**, which, heated with the alkyne **6d** in the presence of Pd_2dba_3, $AsPh_3$ for 5 h, gave complex **8d** in 80% yield.

Crystals of 3,3′-(ethynylbenzenetricarbonylchromium), 2,2′-dimethoxy, and 1,1′-binaphthyl **8a** suitable for X-ray analysis were obtained from a solution of the complex in a petroleum ether/acetone mixture. CAMERON views and some selected bond lengths are presented in Figures 1−3, and crystal data are reported in Table 2. Three important features can be emphasized. First, the neutral complex displays the well-known piano-stool conformation found in half-sandwich tricarbonyl complexes.[2a,d,e] The conformations adopted by the $Cr(CO)_3$ entities with respect to the aromatic carbons of the rings are unexpectedly different for each half of the molecule. One is a staggered conformation of the tripod with dihedral angles $O_{2'}Cr_{1'}CtC_{11'}$, $O_{3'}Cr_{1'}CtC_{15'}$, and $O_{1'}Cr_{1'}CtC_{13'}$ of 26°, 28°, and 31°, respectively, for the tripod coordinated to the $C_{11'}-C_{16'}$ carbons, Ct being the center of the six-membered ring, Figure 2, whereas the other one is an almost eclipsed conformation with dihedral angles $O_{21}Cr_1$-CtC_{11}, $O_{23}Cr_1CtC_{13}$, and $O_{22}Cr_1CtC_{15}$ of 6°, 14°, and 18°, respectively, Figure 1. These differences are probably due to crystal packing effects. It is worthy to note that these two conformations are associated with two opposite orientations of

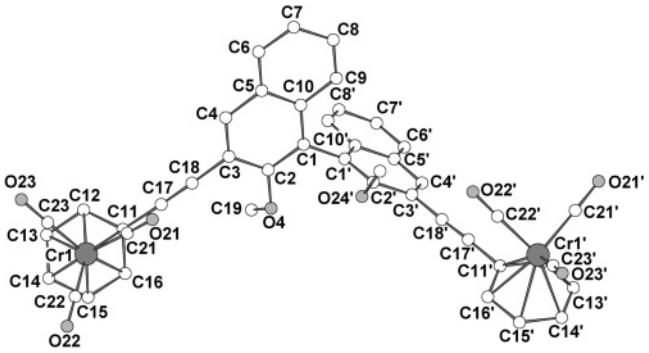


Figure 1. CAMERON views of complex **8a** with the $Cr_1(CO)_3$ tripod projected onto the first arene ring. Selected bond lengths (Å): Cr_1C_{11} 2.177(9); Cr_1C_{12} 2.191(11); Cr_1C_{13} 2.199(12); Cr_1C_{14} 2.182(11); Cr_1C_{15} 2.172(11); Cr_1C_{16} 2.192(10); $C_{11}C_{12}$ 1.385(14); $C_{12}C_{13}$ 1.412(16); $C_{13}C_{14}$ 1.368(16); $C_{14}C_{15}$ 1.377(15); $C_{15}C_{16}$ 1.398(15); $C_{16}C_{11}$ 1.398(13).

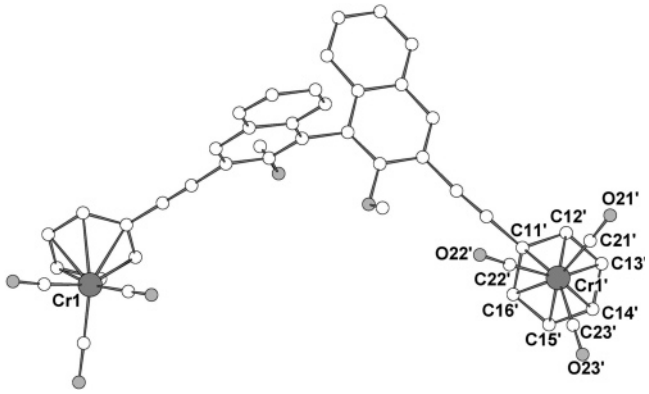


Figure 2. CAMERON views of complex **8a** with the $Cr_{1'}(CO)_3$ tripod projected onto the second arene ring. Selected bond lengths (Å): $Cr_{1'}C_{11'}$ 2.212(8); $Cr_{1'}C_{12'}$ 2.199(8); $Cr_{1'}C_{13'}$ 2.200(9); $Cr_{1'}C_{14'}$ 2.210(10); $Cr_{1'}C_{15'}$ 2.229(8); $Cr_{1'}C_{16'}$ 2.238(8); $C_{11'}C_{12'}$ 1.393(11); $C_{12'}C_{13'}$ 1.414(12); $C_{13'}C_{14'}$ 1.393(13); $C_{14'}C_{15'}$ 1.392(12); $C_{15'}C_{16'}$ 1.412(11); $C_{16'}C_{11'}$ 1.433(11).

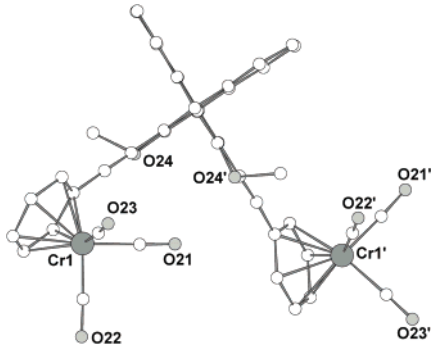


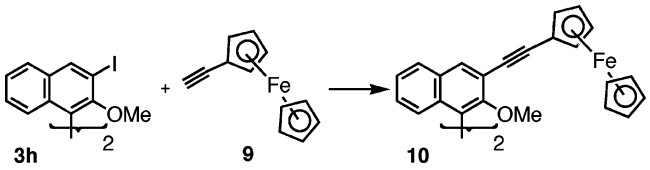
Figure 3. Dihedral angle between the two binaphthyl planes and proximal and distal positions of the MeO groups of complex **8a**.

the methoxy groups of the binaphthyl residue as clearly shown in Figure 3. Indeed, the tripod $Cr(CO)_3$, which is almost eclipsed by the C_{11}, C_{13}, and C_{15} carbon atoms of the arene ring, is associated with a distal methoxy group *anti* to the first Cr atom, and the almost staggered tripod $Cr(CO)_3$ is associated with a proximal methoxy group *syn* to the second Cr atom. Second, the bond lengths of the Cr_1 and the $Cr_{1'}$ atoms to the aromatic carbons have almost the same mean value, 2.185(11) Å (range 2.152−2.218) and 2.215(11) Å (range 2.182−2.248), respectively. The dihedral angle between the naphthyl planes is 88° as expected, Figure 3. This view clearly shows the proximal and distal positions of the methyl of the methoxy groups. Finally,

Table 2. Crystal Data for Complexes 8a ($C_{44}H_{26}Cr_2O_8$) and 17 ($C_{35}H_{28}CrO_7$)

	17	**8a**
formula	$C_{35}H_{28}CrO_7$	$C_{44}H_{26}Cr_2O_8$
cryst class	monoclinic	monoclinic
space group	*C*2/*c*	$P2_1/n$
a (Å)	22.541(5)	10.610(2)
b (Å)	10.630(4)	24.260(7)
c (Å)	26.26(1)	14.354(4)
α (deg)	90	90
β (deg)	111.75(2)	107.98(2)
γ (deg)	90	90
V (Å^3)	5843(4)	3514(1)
Z	8	4
radiation type	Mo Kα	Mo Kα
wavelength (Å)	0.71073	0.71073
density	1.39	1.49
M_r	612.60	786.68
μ (cm^{-1})	0.442	0.676
temp (K)	295	120
size (mm)	0.07 × 0.18 × 0.30	0.03 × 0.15 × 0.45
color	yellow	orange
shape	plate	stick
diffractometer	Nonius KappaCCD	Nonius KappaCCD
no. of rflns measd	14 876	22 217
no of indep rflns	4487	5931
θ (min,max)	1, 25.51	1, 26.02
index ranges		
h	−27 19	−12 12
k	−12 11	−29 26
l	−31 31	−17 17
refinement	on F	on F
$R = \sum(\|F_o\| - \|F_c\|)/\sum\|F_o\|$	0.0744	0.0842
$R_w = [\sum w(\|\|F_o\| - \|F_c\|\|)^2/\sum wF_o^2]^{1/2}$	0.0822	0.0875
$\Delta\rho_{min}$ (e Å^{-3})	−0.44	−1.47
$\Delta\rho_{max}$ (e Å^{-3})	0.73	1.52
no. of rflns used	1529	2885
$\sigma(I)$ limit	3.0	3
no. of params	178	227
GOF	1.144	1.047

Scheme 5. Synthesis of the Dinuclear Complex 10

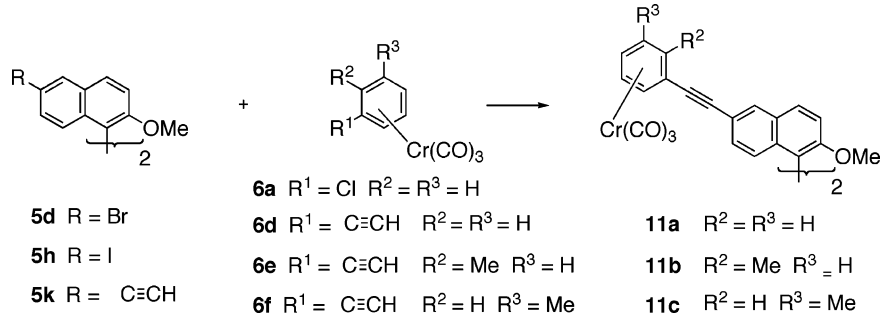


we noticed some $\pi-\pi$ stacking between two naphthyl groups of two different molecules. A distance of 3.4 Å was observed between one naphthyl group of a molecule parallel to another naphthyl group of another molecule. The dihedral angle of the plane of the metal-coordinated arene ring and the corresponding naphthyl moiety is 29° for the complex bearing the Cr_1 and 30° for the complex bearing the Cr_{31} atom.

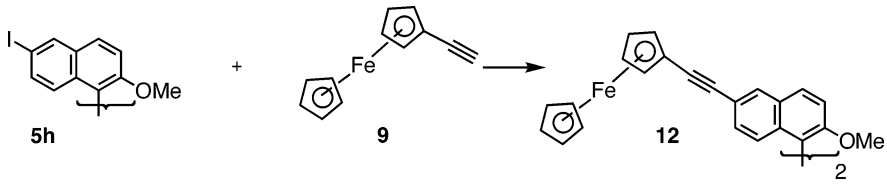
Condensation of the diodo compound **3h** with ethynylferrocene[14] **9** under the same experimental conditions as those used for the formation of **8d** afforded the bis-ferrocenyl complex **10** in 80% yield, Scheme 5. We generalized these reactions with the halogenated binaphthyl derivatives substituted at the C_6 position. We first tried to react the dibromo compound **5d** with ethynylbenzenetricarbonylchromium **6d**[2d,10] and $PdCl_2(PPh_3)_2$, CuI, and Et_3N but without any success. Next, we tested the diiodo compound **5h** obtained in 97% yield by lithiation of **5d** with *n*-BuLi at 78 °C and then by treatment with I_2. Sonogashira coupling in the presence of CuI, $PdCl_2(PPh_3)_2$, and NEt_3 with **6d** afforded the expected yellow complex **11a** in 64% yield, confirming the much stronger reactivity of the iodo derivatives

(14) Polin, J.; Schottenberger, H. *Org. Synth.* **1996**, *73*, 262.

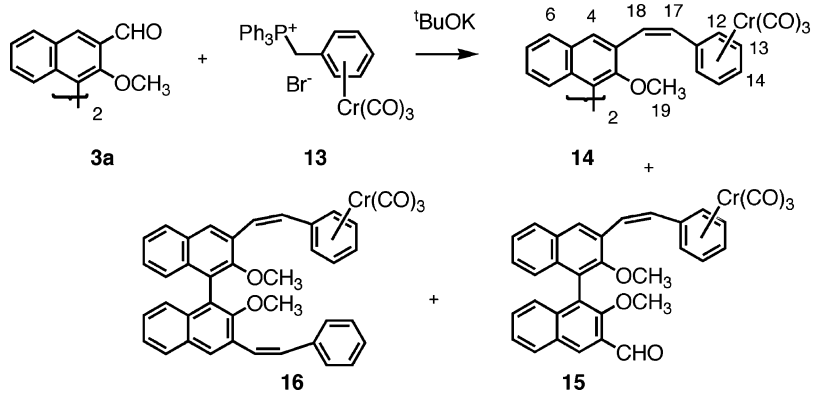
Scheme 6. Synthesis of the Dinuclear Complexes 11



Scheme 7. Synthesis of the Dinuclear Complexes 12



Scheme 8. Synthesis of the Dinuclear Complex 14



in both C3- and C6-substituted series, Scheme 6. We extended this reaction by using *ortho* and *meta* methylethynylbenzenetricarbonylchromium complexes **6e**,**f** and recovered complexes **11b** and **11c** in 57% and 43% yield, respectively, as orange yellow and yellow compounds, Scheme 6. Alternatively, we reacted the 6,6′-bis-ethynylbinaphthyl compound **5k** and chlorobenzenetricarbonylchromium **6a** with a catalytic amount of $PdCl_2(PPh_3)_2$ and CuI, in the presence of NEt_3 to form **11a**, but the less satisfying yield 43% than the preceding one 64% obtained with the triple bond linked to the organometallic partner was in good agreement with the results obtained for the C_3-substituted complex **8a**. Under the same conditions as the ones used for the formation of **10**, ethynylferrocene **9** and the 6,6′-diodo compound **5h** gave the bimetallic iron complex **12** in 69% yield, Scheme 7.

Binaphthyl Derivatives and Arenetricarbonylchromium and Ferrocene Complexes Linked through a Double Bond: Synthesis of 14−17 and 19. The choice of a double bond as a spacer was dictated for a synthetic point of view but also by the pioneering work of Green[15] and Marder et al.,[16] showing interesting properties of a (*Z*)-1-ferrocenyl-2-(4 nitrobenzene)-ethylene crystal and of the iodide of a cationic complex of (*E*)-1-ferrocenyl-2-(4 pyridinium) ethylene, respectively. Thus, we prepared first the η^6-(benzyl)tricarbonylchromiumtriphenylphosphonium bromide **13**[18b] in 68% yield by treating the tricarbonylchromium complex of benzylic alcohol[10] with PPh_3, HBr[17] in THF in the presence of 4 Å molecular sieves.

Condensation of the ylide generated by treating the phosphonium **13** with ^{t}BuOK[18] and the dialdehyde **3a**[7a] in refluxing THF for 4 h afforded three products **14**, **15**, and **16** in 44%, 33%, and 13% yield, respectively, Scheme 8. Unexpectedly, the *Z* dinuclear complex **14** was not contaminated by the *E* conformer. The two olefinic protons H_{17} and H_{18} of complex **14** resonate at 7.03 and 6.33 ppm, and the five aromatic protons of the ring coordinated to the $Cr(CO)_3$ fragment exhibit two signals at 5.33 (H_{13} H_{14} H_{15}, m) and at 5.47 ppm (H_{12} H_{16}, d). The monoaldehyde **15** corresponded to the condensation of only one ylide to the dialdehyde **3a**, and compound **16** was probably recovered by decomplexation by light and (or) air of one of the arene rings of **14**. The chemical shifts of the two sets of olefinic protons of complex **16** are interesting to compare. Indeed, for the double bond linked to the arenetricarbonylchromium complex, the chemical shifts of the H_{17} and H_{18} protons are 6.33 and 7.03 ppm, $J = 12$ Hz, chemical shifts similar to the values noted for complex **14**. Yet for the other double bond conjugated to the phenyl ring, a large 0.47 ppm deshielding was observed for the α proton at 6.80 ppm and a small 0.09 ppm deshielding

(15) Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Baudy, J. A.; Bloor, D.; Kolinsky, P.; Jones, R. J. *Nature* **1987**, *330*, 300.

(16) Marder, S. R.; Perry, J. W.; Schaefer, W. P.; Tiemann, B. G.; Groves, P. C.; Perry, K. J. *PROC. SPIE-Int. Soc. Opt. Eng.* **1989**, *1147*, 108.

(17) Hercovet, A.; Le Corre, M. *Synthesis* **1988**, 157.

(18) (a) Justin Thomas, K. R.; Lin, J. T.; Wen, Y. S. *Organometallics* **2000**, *19*, 1008. (b) Zhang, J.-X.; Dubois, P.; Jérôme, R. *Synth. Commun.* **1996**, *26*, 3091.

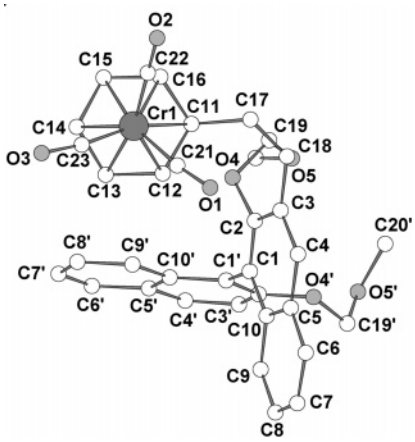


Figure 4. CAMERON view of complex **17-Z** with the $Cr_1(CO)_3$ tripod projected onto the arene ring. Selected bond lengths (Å): CrC_{11} 2.235(11); CrC_{12} 2.188(10); CrC_{13} 2.218(12); CrC_{14} 2.207(13); CrC_{15} 2.227(13); CrC_{16} 2.201(12); $C_{11}C_{12}$ 1.417(14); $C_{12}C_{13}$ 1.409(15); $C_{13}C_{14}$ 1.386(16); $C_{14}C_{15}$ 1.392(16); $C_{15}C_{16}$ 1.401(15); $C_{16}C_{11}$ 1.401(14).

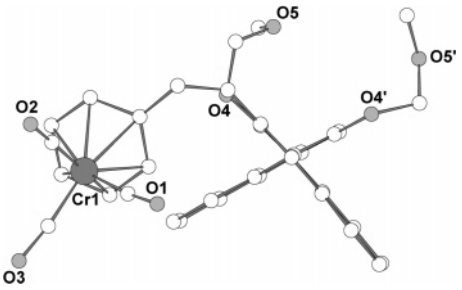
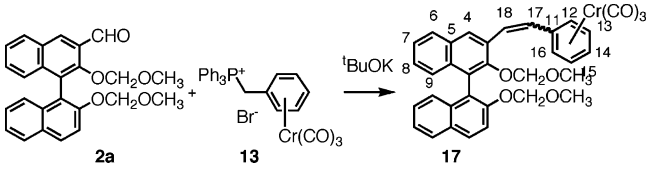


Figure 5. CAMERON view of complex **17-Z** showing the dihedral angle between the binaphthyl groups.

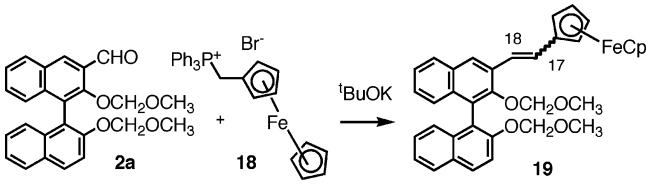
Scheme 9. Synthesis of the Mononuclear Complex 17



for the β proton at 6.95 ppm, corresponding to a more electron-rich olefin due to the decoordination of the $Cr(CO)_3$ entity.

To selectively synthesize a binaphthyl complex monosubstituted by the styrene chromium derivative, we chose the monoaldehyde **2a**[19] as the starting material, taking advantage of its easy and selective formation from the diether **2b**. We reacted the ylide of **13** with the aldehyde **2a** and obtained the *Z* and *E* olefins **17-E** and **17-Z** in 15% and 66% yield, respectively, Scheme 9. Toluenetricarbonylchromium complex was recovered as a byproduct in 3% yield and characterized by NMR spectroscopy.[20] Its formation can be explained by hydrolysis of the phosphorus hydroxide $ArCr(CO)_3CH_2Ph_3P{-}OH$ into $Ph_3P{=}O$ and the benzylic carbanion, which is protonated into the toluene Cr complex. The *Z* and the *E* isomers could be separated by silica gel chromatography column as yellow and orange compounds. The last more intense color might be explained by the conjugation of the π-system of the *E* isomer probably being better than the one for the *Z* isomer.

Scheme 10. Synthesis of the Mononuclear Complex 19



^{1}H NMR data confirm the *Z* and *E* nature of the double bonds. Indeed, the *Z* ethylenic protons resonate at 6.36 and 7.06 ppm, $J = 12$ Hz, whereas for the *E* isomer, one proton is found at 6.93 ppm, $J = 16$ Hz, and the other one is hidden by the fingerprint of the naphthyl proton signal. The chemical shifts of H_{13}, H_{14}, H_{15} *meta* and *para* aromatic protons of the coordinated ring resonate as a multiplet at the same frequency 5.33 ppm, whereas H_{12} and H_{16} *ortho* protons show a doublet at 5.47 ppm, $J = 6$ Hz. These data are in good agreement with an *anti*-eclipsed conformation of the tripod of the major conformer in solution with respect to the double bond.[13]

Crystals of the isomer **17-Z** were obtained by slow diffusion of petroleum-ether into an acetone solution of the complex, which confirmed the *Z* olefin configuration. Crystal data are reported in Table 2, and Figures 4 and 5 show CAMERON views of the complex along with some selected bond lengths. It is worthy to note a nearly *anti*-eclipsed conformation of the $Cr(CO)_3$ tripod with respect to the double bond in the solid state, the dihedral angles of the projected Cr−CO with respect to the aromatic carbon atoms being equal to 14−20°, Figure 4. The MOM group OCH_2OCH_3 adopts a position that avoids interactions with the arenetricarbonylchromium part. The bond lengths $Cr{-}C_i$ ($i = 11{-}16$) between the Cr atom and the carbons of the coordinated ring are almost equal, mean value 2.213(11) Å. The length of the double bond is 1.324(14) Å. Furthermore, the dihedral angle between the arene bearing the chromium entity and the corresponding binaphthyl entity is 115.2°. These two features rule out a strong conjugation between the two aromatic parts in the solid state. We observed an unexpected small dihedral angle between the naphthyl groups of 78°, Figure 5, and some $\pi{-}\pi$ stacking between naphthyl groups of two molecules lying at 3.6 Å.

For the *E* isomer, the H_{12}, H_{13}, and H_{14} protons resonate at frequencies that are much more differentiated than the ones in the *Z* isomer. Indeed, the H_{12}, H_{16} protons resonate at 5.67 ppm, d, $J = 6$ Hz, whereas the $H_{13}H_{15}$ and H_{14} protons resonate at 5.50, t, $J = 6$ Hz and 5.36 ppm, t, $J = 6$ Hz, respectively.

Finally, we undertook a Wittig reaction between the ferrocenyl ylide[21] of **18** and the monoaldehyde **2a**, which afforded the mononuclear iron complex **19** (Table 3) in 45% yield. The *Z* isomer was the major isomer, the ratio *E*:*Z* being 1:3, Scheme 10. We recovered also methylferrocene as a byproduct (5%) whose formation can be explained with the same mechanism as the one involved for toluenetricarbonylchromium complex formation vide supra.

Conclusion

We have developed an efficient strategy to substitute binaphthyl derivatives with (η^6-arene)tricarbonylchromium and ferrocene complexes. Thus, palladium-catalyzed coupling of 3,3′ and 6,6′-boronic acid-2,2′-dialkoxy-1,1′-binaphthtyl and chloroarenetricarbonylchromium derivatives yielded (η^6-arene)-

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(21) (a) Dotsevi, G.; Sogah, Y.; Cram, D. J. *J. Am. Chem. Soc*. **1979**, *11*, 3035. (b) Ostrowski, J.; Hudack, R. A.; Robinson, M. R.; Wang, S.; Bazan, G. C. *Chem.-Eur. J*. **2001**, *7*, 4500.

Table 3. Selected ^{1}H NMR Data of Complexes 14, 15, 17, and 19

complex	H_4	H_6	H_7	H_8	H_9	H_{12}	H_{13}	H_{14}	H_{17}	H_{18}
14	7.97	7.83	7.33	7.45	7.20	5.30	5.45	5.30	6.33[a]	7.03[a]
15	8.02	7.83[i]	7.25−7.49[b]			5.31−5.44[b]			6.34	7.10[c]
	8.63	8.20				7.41	7.28		6.80[a]	6.95[a]
	7.93	7.80								
	7.93	7.69	7.60−7.20[b]			5.30	5.45	5.30	6.33[a]	7.03[a]
17E	8.23	7.93	7.19−7.49			5.67	5.50	5.36	6.93	*d*
	8.01	7.92[g]	7.19−7.49							
17Z	7.92	7.93	7.21−7.45[b]			5.47	5.28−5.37		6.36[a]	7.06[a]
	8.02	7.78	7.21−7.45[b]							
19E	8.08	7.82	7.07−7.29[b]						*d*	7.05
	7.88	7.69								
19Z	7.93	7.78	7.07−7.29[b]						6.40[a]	6.62[a]
	7.87	7.69[h]	7.07−7.29[b]							

[a] or. [b] m. [c] J = 12 Hz. [d] Under naphthyl fingerprint. [e] 5.28−5.37. [f] $H_{3'}$ 7.63. [g] $H_{3'}$ 7.60. [h] $H_{3'}$ 7.50. [i] CHO 10.59.

tricarbonylchromium complexes directly linked to the binaphthyl residue. Coupling reactions of 3,3′ and 6,6′-diiodo-2,2′-dialkoxy-1,1′-binaphthtyl derivatives with ethynylarenetricarbonylchromium and ethynylferrocene complexes yielded (η^6-arene)-tricarbonylchromium and ferrocene complexes linked to binaphthyl derivatives via a triple bond. Similarly, condensing methyltriphenylphosphonium bromide of arenetricarbonylchromium and ferrocene with binaphthylaldehydes afforded complexes with a double bond as spacer. X-ray analyses of two chromium complexes with a double and a triple bond as spacers were also presented, showing clearly the conformations of the tricarbonyl tripods with respect to the aromatic rings.

Experimental Section

General Procedures. All reactions and manipulations were routinely performed under a dry nitrogen atmosphere using Schlenk tube techniques. THF and diethyl ether were dried over sodium benzophenone ketyl and distilled. CH_2Cl_2 was dried over calcium hydride and distilled. Infrared spectra were measured on a Perkin-Elmer 1420 spectrometer. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were obtained on a Bruker AC200, ARX400, or DRX500 spectrometer. Elemental analyses were performed by Le Service de Microanalyses de l'Université Pierre et Marie Curie.

Synthesis of 2,2′-Dimethoxy-3-η^6-(phenyltricarbonylchromium)-1,1′-binaphthyl (3e). 2,2′-Dimethoxy-1,1′-binaphthyl-3,3′-boronic acid, **3g** (0.2 g; 0.50 mmol), chlorobenzene tricarbonylechromium (0.273 g; 1.1 mmol), K_2CO_3 (0.207 g; 1.5 mmol), and $Pd(PPh_3)_4$ (0.029 g; 0.025 mmol) in 15 mL of acetone were introduced in a flask under N_2. The reaction mixture was heated for 21 h under reflux and filtered on Celite. After evaporation of the solvents, the crude mixture was purified by silica gel 15−40 μm chromatography column (petroleum ether/Et_2O: 6/4, 300 mL then PE/Et_2O: 4/6). Complex **3e** (0.105 g) was obtained as an orange solid in 28% yield. ^{1}H NMR (200 MHz, $CDCl_3$): 3.18 (s, 6H, H_{15}), 5.60 (m, 4H, H_{10}, H_{14}), 6.01 (m, 6H, H_{11}, H_{12}, H_{13}), 7.27-7.41-7.75-7.99 (m, 8H, H_5, H_6, H_7, H_8), 8.11 (s, 2H, H_4). IR (neat, cm^{-1}): 1863, 1956 (CO). Anal. Calcd for $C_{40}H_{26}Cr_2O_8$: C, 65.04; H, 3.55. Found: C, 65.21; H, 3.61. MS (FAB m/z): calcd, 738.0; found, 738.0 (M^+).

Synthesis of *o*-Ethynyltoluene Tricarbonylchromium (6e). In a flask, 2-chlorotoluenetricarbonylchromium (0.610 g, 2.32 mmol), CuI (0.023 g, 0.012 mmol), and $PdCl_2(PPh_3)_2$ (0.085 g, 0.012 mmol) were dissolved in 20 mL of THF and 10 mL of Et_3N. At room temperature, ethynyltrimethylsilane (0.50 mL, 3.52 mmol) in 10 mL of THF was slowly added. The resulting mixture was then refluxed for 6 h. After being cooled, the dark solution was filtered through Celite, and the solvents were evaporated under reduced pressure. The orange oil was purified by a silica gel chromatography column (15−40 μm, eluant EP/Et_2O: 96/4). The silylated complex **6e**, **R:CC−SiMe$_3$**, was obtained as an orange solid in 99% yield (0.745 g). ^{1}H NMR (200 MHz, $CDCl_3$): 0.16 (s, 9H, H_{10}), 2.22 (s, 3H, H_7), 5.05 (td, J = 6.2 Hz, J = 1.0 Hz, 1H, H_5), 5.11 (d, J = 6.2 Hz, 1H, H_6), 5.24 (td, J = 6.2 Hz, J = 1.0 Hz, 1H, H_4), 5.49 (d, J = 6.2 Hz, 1H, H_3). ^{13}C NMR (50 MHz, $CDCl_3$): 0.0 (C_{10}), 19.9 (C_7), 88.9 (C_6), 89.6 (C_9), 91.9 (C_8), 92.3−96.5 (C_4, C_5), 98.4 (C_3), 99.6 (C_1), 110.6 (C_2), 232.4 (CO). Anal. Calcd for $C_{15}H_{16}CrO_3Si$: C, 55.55; H, 4.98. Found: C, 55.71; H, 5.03. The silylated complex (3.02 g, 9.7 mmol) was dissolved in 60 mL of methanol. A 2 N aqueous solution of sodium hydroxide (10.7 mL, 21.3 mmol) was added, and the mixture was stirred for 3 h. After 30 mL of water was added, the solution was extracted with 3 × 50 mL of diethyl ether. The organic layers were dried over anhydrous magnesium sulfate, filtered through Celite, and the solvents were evaporated under reduced pressure. Compound **6e** was purified by a short silica gel chromatography column (15−40 μm, eluant EP/Et_2O: 96/4) and obtained as a yellow solid in 87% yield (2.13 g). F = 80 °C. ^{1}H NMR (200 MHz, $CDCl_3$): 2.25 (s, 3H, H_7), 3.00 (s, 1H, H_9), 5.05 (dd, J = 6.0 Hz, J = 0.9 Hz, 1H, H_6), 5.10 (t, J = 6.0 Hz, 1H, H_5), 5.30 (td, J = 6.0 Hz, J = 0.9 Hz, 1H, H_4), 5.55 (dd, J = 6.0 Hz, J = 0.9 Hz, 1H, H_3). ^{13}C NMR (50 MHz, $CDCl_3$): 19.8 (C_7), 78.6 (C_9), 80.1 (C_1), 87.9 (C_8), 88.7-91.7-93.0-96.9 (C_3, C_4, C_5, C_6), 111.1 (C_2), 232.1 (CO). Anal. Calcd for $C_{12}H_8CrO_3$: C, 57.15; H, 3.20. Found: C, 57.01; H, 3.02.

Synthesis of *m*-Ethynyltoluene Tricarbonylchromium (6f). The same methodology as **6e** was used to obtained complex **6f**. **Silylated-6f** (86%), ^{1}H NMR (200 MHz, $CDCl_3$): 0.21 (s, 9H, H_{10}), 2.12 (s, 3H, H_7), 5.03 (d, J = 6.8 Hz, 1H, H_4), 5.23 (d, J = 6.8 Hz, 1H, H_6), 5.25 (s, 1H, H_2), 5.37 (t, J = 6.8 Hz, 1H, H_5). ^{13}C NMR (50 MHz, $CDCl_3$): 0.0 (C_{10}), 20.6 (C_7), 90.6 (C_8), 91.9 (C_6), 93.0 (C_2), 94.9−96.5 (C_4–C_5), 98.4 (C_9), 100.6 (C_1), 111.6 (C_3), 232.6 (CO). Anal. Calcd for $C_{15}H_{16}CrO_3Si$: C, 55.55; H, 4.98. Found: C, 55.67; H, 5.14. **6f** (99%): F = 90 °C. ^{1}H NMR (200 MHz, $CDCl_3$): 2.12 (s, 3H, H_7), 2.89 (s, 1H, H_9), 5.02 (d, J = 6.2 Hz, 1H, H_6), 5.22 (d, J = 6.2 Hz, 1H, H_4), 5.23 (s, 1H, H_2), 5.32 (t, J = 6.2 Hz, 1H, H_5). ^{13}C NMR (50 MHz, $CDCl_3$): 20.6 (C_7), 77.8 (C_1), 79.7 (C_9), 89.9 (C_8), 91.1 (C_2), 92.3 (C_5), 92.6−95.2 (C_4–C_6), 107.9 (C_3), 232.3 (CO). IR (neat): 1870, 1957 (CO), 2165 (C_8C_9). Anal. Calcd for $C_{12}H_8CrO_3$: C, 57.15; H, 3.20. Found: C, 57.06; H, 3.03.

Synthesis of 6,6′-Di(phenyltricarbonylchromium)-2,2′-dimethoxy-1,1′-binaphthyl (7a). In a 50 mL two-necked flask, compound **5g** (0.201 g, 0.5 mmol), chlorobenzene tricarbonylchromium (0.264 g, 1.1 mmol), $Pd(PPh_3)_4$ (0.030 g, 0.025 mmol), and Na_2CO_3 (0.212 g, 2.0 mmol) were placed in 10 mL of methanol and 1.0 mL of water. The solution was heated to reflux. After 0.5 h, the mixture was cooled to room temperature, and the solvents were evaporated under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2 and dried over anhydrous $MgSO_4$, then filtered through Celite, and the solvent was evaporated under reduced pressure. Compound **7a** was obtained as a yellow solid in 71% yield (262 mg). F_{dec} = 197 °C. ^{1}H NMR (200 MHz, $CDCl_3$): 3.79 (s, 6H, OMe), 5.34 (t, J = 6 Hz, 2H, H_{14}), 5.49 (t, J = 6 Hz, 4H,

H_{13} and H_{15}), 5.77 (d, $J = 6$ Hz, 4H, H_{12} and H_{16}), 7.13 (d, $J = 9$ Hz, 2H, H_9), 7.32 (d, $J = 9$ Hz, 2H, H_8), 7.49 (d, $J = 9$ Hz, 2H, H_3), 8.01 (s, 2H, H_6), 8.02 (d, $J = 9$ Hz, 2H, H_4). ^{13}C NMR (100 MHz, $CDCl_3$): 56.7 (OMe), 91.5 (C_{14}), 92.2 (C_{12}, C_{16}), 92.3 (C_{11}), 92.5 (C_{13}, C_{15}), 114.7 (C_3), 125.2 (C_9), 125.9 (C_8), 126.4 (C_4), 130.0 (C_6), 155.8 (C_2), 232.8 (CO), 118.9, 128.7, 131.3, 133.9 (C_1, C_5, C_7, C_{10}). IR (neat, cm^{-1}): 1952, 1847 (CO). UV−vis (CH_3CN) $\lambda = 271$ nm, $\epsilon = 64\,200$, $\lambda = 321$ nm, $\epsilon = 28\,600$ L mol^{-1} cm^{-1}; (CH_2Cl_2) $\lambda = 276$ nm, $\epsilon = 79\,400$ L mol^{-1} cm^{-1}. Anal. Calcd for $C_{40}H_{26}Cr_2O_8$: C, 65.04; H, 3.55. Found: C, 65.01; H, 3.61.

Synthesis of 6,6′-Di(2-methylphenyltricarbonylchromium)-2,2′-dimethoxy-1,1′-binaphthyl (7b). Compound **7b** was synthesized using the same methodology as **7a** starting from 2-chlorotoluene tricarbonylchromium (0.288 g, 1.1 mmol). It was obtained as a yellow solid in 74% yield (284 mg). $F_{dec} = 159$ °C. ^{1}H NMR (200 MHz, $CDCl_3$): 2.16 (s, 6H, H_{17}), 3.81 (s, 6H, OMe), 5.18 (m, 4H, H_{13} and H_{15}), 5.50 (t, $J = 6$ Hz, 2H, H_{14}), 5.62 (d, $J = 6$ Hz, 2H, H_{16}), 7.12 (d, $J = 9$ Hz, 2H, H_9), 7.23 (d, $J = 9$ Hz, 2H, H_8), 7.51 (d, $J = 9$ Hz, 2H, H_3), 7.88 (s, 2H, H_6), 8.02 (d, $J = 9$ Hz, 2H, H_4). ^{13}C NMR (100 MHz, $CDCl_3$): 20.0 (C_{17}), 56.7 (OMe), 88.3 (C_{15}), 91.7 (C_{12}), 114.7 (C_3), 125.2 (C_9), 125.4 (C_8), 129.6 (C_4), 129.8 (C_6), 155.6 (C_2), 233.3 (CO), 110.0, 113.0 (C_{11}, C_{13}), 119.0, 128.5, 131.5, 133.4 (C_1, C_5, C_7, C_{10}). IR (neat, cm^{-1}): 1952, 1859 (CO). UV−vis (CH_3CN) $\lambda = 271$ nm, $\epsilon = 42\,400$, $\lambda = 321$ nm, $\epsilon = 21\,250$ L mol^{-1} cm^{-1}; (CH_2Cl_2) $\lambda = 275$ nm, $\epsilon = 79\,000$ L mol^{-1} cm^{-1}. Anal. Calcd for $C_{42}H_{30}Cr_2O_8$: C, 65.80; H, 3.94. Found: C, 66.01; H, 4.07.

Synthesis of 6,6′-Di(3-methylphenyltricarbonylchromium)-2,2′-dimethoxy-1,1′-binaphthyl (7c). Compound **7c** was synthesized using the same methodology as **7a** starting from 3-chlorotoluene tricarbonylchromium (0.288 g, 1.1 mmol). It was obtained as a yellow solid in 72% yield (276 mg). $F_{dec} = 167$ °C. ^{1}H NMR (200 MHz, $CDCl_3$): 2.29 (s, 6H, H_{17}), 3.79 (s, 6H, OMe), 5.17 (d, $J = 3$ Hz, 2H, H_{12}), 5.58 (m, 6H, H_{14}, H_{15}, H_{16}), 7.13 (d, $J = 9$ Hz, 2H, H_9), 7.33 (d, $J = 9$ Hz, 2H, H_8), 7.49 (d, $J = 9$ Hz, 2H, H_3), 8.01 (s, 2H, H_6), 8.02 (d, $J = 9$ Hz, 2H, H_4). ^{13}C NMR (100 MHz, $CDCl_3$): 20.9 (C_{17}), 56.7 (OMe), 89.3 (C_{16}), 91.4 (C_{12}), 92.7 (C_{15}), 94.1 (C_{14}), 114.7 (C_3), 125.3 (C_9), 125.8 (C_8), 126.6 (C_4), 130.0 (C_6), 155.7 (C_2), 233.3 (CO), 109.2, 112.1 (C_{11}, C_{13}), 118.9, 128.6, 131.4, 133.9 (C_1, C_5, C_7, C_{10}). IR (neat, cm^{-1}): 1951, 1860 (CO). UV−vis (CH_3CN) $\lambda = 273$ nm, $\epsilon = 60\,000$, $\lambda = 321$ nm, $\epsilon = 29\,400$ L mol^{-1} cm^{-1}; (CH_2Cl_2) $\lambda = 274$ nm, $\epsilon = 73\,700$ L mol^{-1} cm^{-1}. Anal. Calcd for $C_{42}H_{30}Cr_2O_8$: C, 65.80; H, 3.94. Found: C, 65.91; H, 4.01.

Synthesis of 2,2′-Dimethoxy-3,3′-di(phenylethynyltricarbonylchromium)-1,1′-binaphthyl (8a). In a flask, compound **3h** (0.283 g, 0.50 mmol) and complex **6d**[2c,d] (0.262 g, 1.1 mmol), Pd_2dba_3 (0.023 g, 0.025 mmol), and $AsPh_3$ (0.023 g, 0.075 mmol) were dissolved in 15 mL of Et_3N distilled and kept over KOH. The mixture was heated at 40 °C for 6 h. The dark solution was then filtered trough Celite at room temperature, and the solvent was evaporated under reduced pressure. Compound **8a** was purified by silica gel chromatography column (15−40 μm, eluant EP/Et_2O: 6/4, 300 mL and then 4/6) and obtained as an orange solid in 74% yield (0.291 g). $F = 210$ °C. ^{1}H NMR (200 MHz, $CDCl_3$): 3.65 (s, 6H, H_{19}), 5.34 (m, 6H, H_{13}, H_{14}, H_{15}), 5.60 (m, 4H, H_{12}, H_{16}), 7.10 (d, $J = 8.0$ Hz, 2H, H_9), 7.28 (td, $^3J = 8.0$ Hz, $^4J = 1.3$ Hz, 2H, H_8), 7.42 (td, $^3J = 8.0$ Hz, $^4J = 1.3$ Hz, 2H, H_7), 7.86 (d, $^3J = 8.0$ Hz, 2H, H_6), 8.20 (s, 2H, H_4). ^{13}C NMR (50 MHz, $CDCl_3$): 61.4 (C_{19}), 86.6-89.5-90.1 ($C_{11-}C_{17-}C_{18}$), 91.1 (C_{14}), 91.3 (C_{12}, C_{16}), 95.1 (C_{13}, C_{15}), 115.9 (C_1), 124.8 (C_3), 125.5 (C_7, C_9), 127.7−127.9 (C_6, C_8), 130.0 (C_{10}), 134.0 (C_5), 134.9 (C_4), 155.5 (C_2), 232.1 (CO). IR (neat): 1889, 1966 (CO); 2364 ($C_{17}-C_{18}$). UV−visible (CH_2Cl_2) λ 279 ($\epsilon = 58\,930$ L mol^{-1} cm^{-1}); λ 305 ($\epsilon = 41\,300$ L mol^{-1} cm^{-1}); λ 409 ($\epsilon = 4970$ L mol^{-1} cm^{-1}); (CH_3CN) λ 274 ($\epsilon = 44\,100$ L mol^{-1} cm^{-1}); λ 302 ($\epsilon = 34\,100$ L mol^{-1} cm^{-1}); λ 406 ($\epsilon = 7445$ L mol^{-1} cm^{-1}). MS (FAB, *m*/*z*): calcd 786.0 (found: 786.1). Anal. Calcd for $C_{44}H_{26}Cr_2O_8$: C, 67.17; H, 3.33. Found: C, 67.31; H, 3.55.

Synthesis of 2,2′-Dimethoxy-3,3′-di(*o*-tolylethynyltricarbonylchromium)-1,1′-binaphthyl (8b). The same methodology as the one for **8a** was used. Compound **8b** was obtained as an orange solid in 60% yield. $F = 138$ °C. ^{1}H NMR (200 MHz, $CDCl_3$): 2.46 (s, 3H, H_{20}), 3.66 (s, 6H, H_{19}), 5.18 (t, $J = 6.3$ Hz, 2H, H_{15}), 5.23 (m, 2H, H_{16}), 5.41 (m, 2H, H_{14}), 5.77 (m, 2H, H_{13}), 7.12 (d, $J = 8.0$ Hz, 2H, H_9), 7.29 (t, $J = 8.0$ Hz, 2H, H_8), 7.43 (t, $J = 8.0$ Hz, 2H, H_7), 7.88 (d, $J = 8.0$ Hz, 2H, H_6), 8.22 (s, 2H, H_4). ^{13}C NMR (50 MHz, C_6D_6): 19.8 (C_{20}), 61.3 (C_{19}), 88.7 (C_{16}), 89.5−89.2 ($C_{11-}C_{17-}C_{18}$), 91.8 (C_{13}), 92.8 (C_{15}), 95.1 (C_{12}, C_{14}), 116.8 (C_1), 125.7 (C_3), 125.8−126.1 (C_7,C_9), 128.2 (C_6, C_8), 130.6 (C_{10}), 134.7 (C_5), 135.1 (C_4), 156.3 (C_2), 232.0 (CO). IR (neat): 1880, 1960 (CO); 2210 ($C_{17}-C_{18}$). MS (FAB, *m*/*z*): calcd 814.2 (found: 814.1). UV−vis (CH_3CN) $\lambda = 273$ nm, $\epsilon = 77\,100$; (CH_2Cl_2) $\lambda = 280$ nm, $\epsilon = 77\,220$, $\lambda = 309$ nm, $\epsilon = 47\,500$, $\lambda = 327$ nm, $\epsilon = 45\,210$ L mol^{-1} cm^{-1}. Anal. Calcd for $C_{46}H_{30}Cr_2O_8$: C, 67.81; H, 3.71. Found: C, 67.59; H, 3.53.

Synthesis of 2,2′-Dimethoxy-3,3′-di(*m*-tolylethynyltricarbonylchromium)-1,1′-binaphthyl (8c). The same methodology as the one for **8a** was used. Compound **8c** was obtained as an orange solid in 90% yield. $F = 146$ °C. ^{1}H NMR (200 MHz, $CDCl_3$): 2.16 (s, 3H, H_{20}), 3.65 (s, 6H, H_{19}), 5.05 (m, 2H, H_{12}), 5.36 (m, 6H, H_{14}, H_{15}, H_{16}), 7.03 (d, $J = 8.0$ Hz, 2H, H_9), 7.21 (t, $J = 8.0$ Hz, 2H, H_8), 7.35 (t, $J = 8.0$ Hz, 2H, H_7), 7.79 (d, $J = 8.0$ Hz, 2H, H_6), 8.13 (s, 2H, H_4). ^{13}C NMR (50 MHz, C_6D_6): 20.1 (C_{20}), 61.4 (C_{19}), 87.5−90.2 ($C_{17-}C_{18}$), 90.8 (C_{12}), 91.8 (C_{13}), 91.9 (C_{16}), 92.8 (C_{14}), 94.9 (C_{15}), 108.1 (C_{11}), 116.6 (C_1), 125.7 (C_3), 125.8−126.1 (C_7,C_9), 128.1 (C_6 et C_8), 130.7 (C_{10}), 134.8 (C_5), 135.5 (C_4), 156.4 (C_2), 232.2 (CO). IR (neat): 1879, 1960 (CO); 2218 ($C_{17}-C_{18}$). UV−visible (CH_3CN) λ 274 ($\epsilon = 47\,600$ L mol^{-1} cm^{-1}); λ 307 ($\epsilon = 43\,100$ L mol^{-1} cm^{-1}); λ 322 ($\epsilon = 36\,900$ L mol^{-1} cm^{-1}); (CH_2Cl_2) λ 279 ($\epsilon = 67\,100$ L mol^{-1} cm^{-1}); λ 307 ($\epsilon = 40\,400$ L mol^{-1} cm^{-1}); λ 325 ($\epsilon = 38\,200$ L mol^{-1} cm^{-1}). MS (FAB, *m*/*z*): calcd 814.2 (found: 814.2). Anal. Calcd for $C_{46}H_{30}Cr_2O_8$: C, 67.81; H, 3.71. Found: C, 67.65; H, 3.58.

Synthesis of 2,2′-Dimethoxymethyl-3,3′-di(phenylethynyltricarbonylchromium)-1,1′-binaphthyl (8d). 8d was obtained as a red solid in 80% yield, using the same methodology as the one used for **8a**. $F = 86$ °C. ^{1}H NMR (200 MHz, $CDCl_3$): 3.65 (s, 6H, H_{20}), 4.91 (d, $J = 6.0$ Hz, 2H, H_{19}), 5.11 (d, $J = 6.0$ Hz, 2H, H_{19}), 5.32 (m, 6H, H_{13}, H_{14}, H_{15}), 5.56 (m, 4H, H_{12}, H_{16}), 7.20 (d, $J = 7.0$ Hz, 2H, H_9), 7.32 (td, $J = 7.0$ Hz, $J = 1.3$ Hz, 2H, H_8), 7.42 (td, $J = 7.0$ Hz, $J = 1.3$ Hz, 2H, H_7), 7.86 (d, $J = 7.0$ Hz, 2H, H_6), 8.21 (s, 2H, H_4). ^{13}C NMR (50 MHz, $CDCl_3$): 56.1 (C_{20}), 86.6-89.4-89.8 ($C_{11-}C_{17-}C_{18}$), 91.1 (C_{14}), 91.2 (C_{12}, C_{16}), 95.0 (C_{13}, C_{15}), 115.8 (C_1), 124.8 (C_3), 125.7−126.5 (C_7, C_9), 127.7 (C_6, C_8), 130.1 (C_{10}), 134.0 (C_5), 135.0 (C_4), 152.9 (C_2), 232.0 (CO). IR (neat): 1880, 1962 (CO); 2360 ($C_{17}-C_{18}$). UV−visible (CH_2Cl_2) λ 277 ($\epsilon = 43\,120$ L mol^{-1} cm^{-1}); λ 306 ($\epsilon = 34\,130$ L mol^{-1} cm^{-1}); λ 410 ($\epsilon = 6614$ L mol^{-1} cm^{-1}); (CH_3CN) λ 275 ($\epsilon = 47\,830$ L mol^{-1} cm^{-1}); λ 304 (shoulder); λ 410 ($\epsilon = 7491$ L mol^{-1} cm^{-1}). MS (FAB, *m*/*z*): calcd 846.1 (found: 846.2). Anal. Calcd for $C_{46}H_{30}Cr_2O_{10}$: C, 65.24; H, 3.57. Found: C, 65.37; H, 3.71.

Synthesis of 2,2′-Dimethoxy-3,3′-di(ferrocenylethynyl)-1,1′-binaphthyl (10). The same methodology as the one for **8a** was used. Ethynylferrocene **9** (0.231 g, 1.1 mmol) was used instead of the complex **6d**. Compound **10** was obtained as an orange solid in 80% yield. ^{1}H NMR (200 MHz, $CDCl_3$): 3.72 (s, 6H, H_{19}), 4.25 (m, 14H, H_{13}, H_{14}, H_{16}), 4.54 (m, 4H, H_{12}, H_{15}), 7.11 (d, $J = 7.5$ Hz, 2H, H_9), 7.25 (t, $J = 7.5$ Hz, 2H, H_8), 7.39 (t, $J = 7.5$ Hz, 2H, H_7), 7.84 (d, $J = 7.6$ Hz, 2H, H_6), 8.16 (s, 2H, H_4). ^{13}C NMR (50 MHz, $CDCl_3$): 61.0 (C_{19}), 65.3 (C_{11}), 68.9 (C_{12}, C_{15}), 69.9 (C_{16}), 71.4 (C_{13}, C_{14}), 82.6−92.9 ($C_{17-}C_{18}$), 117.9 (C_1), 124.9 (C_3), 125.2−125.7 ($C_{7-}C_9$), 127.6−128.4 ($C_{6-}C_7$), 130.0 (C_{10}), 133.0 (C_5), 133.5 (C_4), 155.6 (C_2). IR (neat): 2211 ($C_{17}-C_{18}$). UV−visible (CH_2-

Cl_2) λ 266 (ε = 55 908 L mol^{-1} cm^{-1}); λ 290 (sh); λ 443 (ε = 1273 L mol^{-1} cm^{-1}); (CH_3CN) λ 269 (ε = 47 509 L mol^{-1} cm^{-1}); λ 285 (sh); λ 446 (ε = 1156 L mol^{-1} cm^{-1}). MS (FAB, *m*/*z*): calcd 730.1 (found: 730.2). Anal. Calcd for $C_{46}H_{34}Fe_2O_2$: C, 75.60; H, 4.69. Found: C, 75.48; H, 4.52.

Synthesis of 6,6′-Di(phenylethynyltricarbonylchromium)-2,2′-dimethoxy-1,1′-binaphthyl (11a). In a 50 mL two-necked flask, compound **5h** (0.283 g, 0.5 mmol), phenylacetylide tricarbonylchromium, **6d** (0.263 g, 1.1 mmol), $PdCl_2(PPh_3)_2$ (0.018 g, 0.025 mmol), and CuI (0.005 g, 0.025 mmol) were placed in 10 mL of THF and 10 mL of Et_3N. The solution was then refluxed and became red. After 3 h, the mixture was cooled to room temperature and filtered through Celite. The solvents were evaporated under reduced pressure. The residue was purified by silica gel chromatography column (60 μm, eluent cyclohexane/CH_2Cl_2: from 100/0 to 50/50 by portions of 50 mL and increment of 5%) and obtained as a yellow solid in 64% yield (289 mg). F_{dec} = 193 °C. ^{1}H NMR (200 MHz, $CDCl_3$): 3.77 (s, 6H, OMe), 5.25 (t, *J* = 6 Hz, 2H, H_{16}), 5.36 (t, *J* = 6 Hz, 4H, H_{15} and H_{17}), 5.53 (d, *J* = 6 Hz, 4H, H_{14} and H_{18}), 7.02 (d, *J* = 9 Hz, 2H, H_9), 7.26 (d, *J* = 9 Hz, 2H, H_8), 7.46 (d, *J* = 9 Hz, 2H, H_3), 7.95 (d, *J* = 9 Hz, 2H, H_4), 8.06 (d, *J* = 2 Hz, 2H, H_6). ^{13}C NMR (100 MHz, $CDCl_3$): 56.6 (OMe), 84.9 (C_{13}), 90.4 (C_{12}, C_{16}), 91.0 (C_{11}), 91.7 (C_{15}, C_{17}), 94.7 (C_{14}, C_{18}), 114.4 (C_3), 125.2 (C_9), 128.4 (C_8), 128.7 (C_4), 129.7 (C_6), 155.9 (C_2), 232.2 (CO), 114.4, 118.8, 128.3, 133.6 (C_1, C_5, C_7, C_{10}). IR (neat, cm^{-1}): 1873, 1964, (CO). UV−visible (CH_2Cl_2) λ 285 (ε = 86 450 L mol^{-1} cm^{-1}); λ 341 (ε = 37 100 L mol^{-1} cm^{-1}); (CH_3CN) λ 281 (ε = 76 900 L mol^{-1} cm^{-1}); λ 319 (ε = 48 300 L mol^{-1} cm^{-1}). MS (FAB, *m*/*z*): calcd 786.0 (found: 786.1). Anal. Calcd for $C_{44}H_{26}Cr_2O_8$: C, 67.17; H, 3.33. Found: C, 67.41; H, 3.59.

Synthesis of 6,6′-Di(2-methylphenylethynyltricarbonylchromium)-2,2′-dimethoxy-1,1′-binaphthyl (11b). Compound **11b** was synthesized using the same methodology as **11a** and compound **6e** (0.278 g, 1.1 mmol). It was obtained as a yellow solid in 43% yield (175 mg). F_{dec} = 148 °C. ^{1}H NMR (200 MHz, $CDCl_3$): 2.40 (s, 6H, H_{19}), 3.78 (s, 6H, OMe), 5.19 (t, *J* = 6 Hz, 2H, H_{15}), 5.23 (d, *J* = 6 Hz, 2H, H_{16}), 5.35 (t, *J* = 6 Hz, 2H, H_{14}), 5.70 (d, *J* = 6 Hz, 2H, H_{13}), 7.03 (d, *J* = 9 Hz, 2H, H_9), 7.26 (d, *J* = 9 Hz, 2H, H_8), 7.47 (d, *J* = 9 Hz, 2H, H_3), 7.96 (d, *J* = 9 Hz, 2H, H_4), 8.06 (d, *J* = 2 Hz, 2H, H_6). ^{13}C NMR (100 MHz, $CDCl_3$): 26.9 (C_{19}), 56.6 (OMe), 85.0, 90.4, 90.5, 91.1, 91.7, 94.7 (C_{13-18}), 114.6 (C_3), 125.3 (C_9), 128.8 (C_8), 129.7 (C_4), 132.4 (C_6), 156.0 (C_2), 232.2 (CO), 116.6, 119.0, 128.5, 133.7 (C_1, C_5, C_7, C_{10}). IR (neat, cm^{-1}): 1871, 1957 (CO), 2202 ($C_{11}C_{12}$). UV−visible (CH_2Cl_2) λ 276 (ε = 115 000 L mol^{-1} cm^{-1}); λ 321 (ε = 48 200 L mol^{-1} cm^{-1}); (CH_3CN) λ 277 (ε = 90 100 L mol^{-1} cm^{-1}); λ 319 (ε = 48 900 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{46}H_{30}Cr_2O_8$: C, 67.81; H, 3.71. Found: C, 67.52; H, 3.44.

Synthesis of 6,6′-Di(3-methylphenylethynyltricarbonylchromium)-2,2′-dimethoxy-1,1′-binaphthyl (11c). Compound **11c** was synthesized using the same methodology as the one for **11a** starting from compound **6f** (0.278 g, 1.1 mmol). It was obtained as a yellow solid in 57% yield (232 mg). F_{dec} = 117 °C. ^{1}H NMR (200 MHz, $CDCl_3$): 2.22 (s, 6H, H19), 3.77 (s, 6H, OMe), 5.06 (d, *J* = 6 Hz, 2H, H_{16}), 5.38 (m, 6H, H_{14}, H_{17}, H_{18}), 7.03 (d, *J* = 9 Hz, 2H, H_9), 7.26 (d, *J* = 9 Hz, 2H, H_8), 7.46 (d, *J* = 9 Hz, 2H, H_3), 7.95 (d, *J* = 9 Hz, 2H, H_4), 8.00 (d, *J* = 2 Hz, 2H, H_6). ^{13}C NMR (100 MHz, $CDCl_3$): 20.7 (C_{19}), 56.6 (OMe), 77.3 (C_{11}), 85.1 (C_{12}), 90.6 (C_{16}), 91.9 (C_{17}), 92.5 (C_{13}), 93.1 (C_{18}), 94.9 (C_{14}), 108.3 (C_{15}), 114.5 (C_3), 125.2 (C_9), 128.4 (C_8), 128.8 (C_4), 129.7 (C_6), 155.9 (C_2), 232.8 (CO), 116.5, 118.9, 128.5, 133.7 (C_1, C_5, C_7, C_{10}). IR (neat, cm^{-1}): 1871, 1957 (CO), 2213 ($C_{11}C_{12}$). UV−visible (CH_2Cl_2) λ 280 (ε = 115 100 L mol^{-1} cm^{-1}); (CH_3CN) λ 277 (ε = 90 100 L mol^{-1} cm^{-1}); λ 319 (ε = 48 900 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{46}H_{30}Cr_2O_8$: C, 67.81; H, 3.71. Found: C, 67.62; H, 3.49.

Synthesis of 6,6′-Di(ferrocenylethynyl)-2,2′-dimethoxy-1,1′-binaphthyl (12). In a 50 mL two-necked flask, compound **5h** (0.283 g, 0.5 mmol), ethynylferrocene, **9** (0.252 g, 1.2 mmol), $PdCl_2(PPh_3)_2$ (0.018 g, 0.025 mmol), and CuI (0.005 g, 0.025 mmol) were placed in 15 mL of THF and 15 mL of Et_3N. The solution was then refluxed. After 3 h, the mixture was cooled to room temperature and filtered through Celite. The solvents were evaporated under reduced pressure. The residue was washed with a solution of K_2CO_3 to eliminate triethylammonium salts, and compound **12** was purified by crystallization in a hot mixture of CH_2Cl_2 and cyclohexane. It was obtained as a brown solid in 69% yield (252 mg). F_{dec} = 161 °C. ^{1}H NMR (200 MHz, $CDCl_3$): 3.77 (s, 6H, OMe), 4.23 (m, 14H, H_{18}, H_{15}, H_{16}), 4.51 (m, 4H, H_{14}, H_{17}), 7.03 (d, *J* = 9 Hz, 2H, H_9), 7.26 (d, *J* = 9 Hz, 2H, H_8), 7.45 (d, *J* = 9 Hz, 2H, H_3), 7.93 (d, *J* = 9 Hz, 2H, H_4), 8.02 (d, *J* = 2 Hz, 2H, H_6). ^{13}C NMR (100 MHz, $CDCl_3$): 56.7 (OMe), 65.5 (C_{13}), 68.7 (C_{15}, C_{16}), 69.9 (C_{18}), 71.3 (C_{14}, C_{17}), 86.2, 88.0 (C_{11}, C_{12}), 114.5 (C_3), 125.1 (C_9), 128.9 (C_8), 129.3 (C_4), 131.0 (C_6), 155.4 (C_2). IR (neat, cm^{-1}): 2208 ($C_{11}C_{12}$). UV−visible (CH_2Cl_2) λ 273 (ε = 71 900 L mol^{-1} cm^{-1}); λ 321 (ε = 44 300 L mol^{-1} cm^{-1}); (CH_3CN) λ 271 (ε = 75 700 L mol^{-1} cm^{-1}); λ 321 (ε = 36 500 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{46}H_{34}Fe_2O_2$: C, 75.64; H, 4.69. Found: C, 75.36; H, 4.47.

Synthesis of η⁶-(Benzyltricarbonylchromium)triphenylphosphonium Bromide (13). In a flask equipped with a Dean−Stark apparatus, tricarbonylchromiumbenzylalcohol (0.448 g, 2.0 mmol) and triphenylphosphonium hydrobromide (0.618 g, 1.8 mmol) were dissolved in CH_2Cl_2 (30 mL) under N_2. The solution was refluxed for 2 h and heated until dryness over 30 min. The resulting solid was dissolved in CH_2Cl_2 (15 mL) and precipitated by adding dry diethyl ether (10 mL per amount until persistence of the yellow precipitate). After decanting, the liquid layer was removed with a syringe and the solid was washed twice with 10 mL of dry diethyl ether. After being dried under reduced pressure, compound **13** was obtained as a yellow solid in 68% yield (0.696 g). ^{1}H NMR (400 MHz, $CDCl_3$): 5.03 (d, *J* = 13 Hz, 2H, CH_2), 5.18 (s large, 3H, ArCr), 5.38 (s arge, 2H, ArCr), 7.71−7.83 (m, 15H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): 59.4 (CH_2), 90.8 (C_{para}-ArCr), 91.5 (C_{ortho}ArCr), 93.2 ($C_{méta}$ArCr), 97.8 (C_{ipso}ArCr), 115.6 (d, *J* = 85 Hz, C_{ipso}Ph), 129.6 (d, *J* = 13 Hz, C_{meta}Ph), 133.5 (d, *J* = 10 Hz, C_{para}Ph), 134.7 (d, *J* = 2.6 Hz, C_{para}Ph), 230.8 (CO). ^{31}P NMR (160 MHz, $CDCl_3$): 24.1. IR (neat): 1858, 1885, 1955 (CO). MS (MALDI-TOF, *m*/*z*): calcd for $C_{28}H_{22}CrO_3P^+$, 489; found, 489 (C^+), 1058 (M + 1 + C^+). Anal. Calcd for $C_{28}H_{22}CrO_3PBr$: C, 59.16; H, 3.90. Found: C, 59.01; H, 3.79.

Synthesis of 2,2′-Dimethoxy-3,3′-η⁶-(ethenylphenyltricarbonylchromium)-1,1′-binaphthyl (14). 3,3′-Diformyl-2,2′-dimethoxy-1,1′-binaphthyl[7a] (0.129 g, 0.35 mmol) in THF (20 mL) and *t*-BuOK (0.77 mL, 0.77 mmol) were introduced into a flask under N_2 and stirred at room temperature for 1 h. Next, the phosphonium **13** (0.40 g, 0.77 mml) was added, and the orange solution was heated for 4 h under reflux. At room temperature, NH_4Cl (20 mL) and 10 mL of Et_2O were added. The aqueous phase was extracted by Et_2O (3 × 40 mL). The organic phase was dried over $MgSO_4$ and filtered on Celite. The solvent was removed under reduced pressure. The crude product was purified on a silica gel chromatography column (Merck silica gel 60, 15−40 μm, petroleum ether/AcOEt 8/2). After evaporation under reduced pressure and drying in vacuo, three complexes were obtained: the dinuclear complex **14**, 0.122 g, in 44% yield, the mononuclear complex **15**, 0.067 g, in 33% yield. The third one recovered in 13% yield corresponded to the decoordination of one of the $Cr(CO)_3$ entities of **14**.

Complex 14. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.97 (s, 2H, H_4), 7.81 (d, *J* = 7.5, 2H, H_6), 7.44 (m, 2H, H_8), 7.35 (m, 2H, H_7), 7.21 (d, *J* = 8.3, 2H, H_9), 7.03 (d, *J* = 12, 2H, H_{17}), 6.33 (d, *J* = 12, 2H, H_{18}), 5.47−5.28 (m, 10H, ArCr), 3.50 (s, 6H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 232.8 (CO−Cr), 154.3 (C_2), 133.8,

130.3, 129.5, 125.3 (C_1, C_3, C_5, C_{10}), 130.1 (C_4), 128.9 (C_{12}), 128.1 (C_6), 127.8 (C_{13}), 126.8 (C_7), 125.5 (C_9), 125.2 (C_8), 105.4 (C_{14}), 93.5, 93.2, 92.2, 92.0, 91.6 (ArCr), 61.3 (C_{11}). IR (neat): ν (cm^{-1}) 1872, 1958 (CO−Cr). UV (CH_3CN): λ 272 nm (ϵ 86 100 L mol^{-1} cm^{-1}). UV (CH_2Cl_2): λ 273 nm (ϵ 139 600 L mol^{-1} cm^{-1}). MS (MALDI-TOF, *m*/*z*): calcd for $C_{44}H_{30}Cr_2O_8$, 790.1; found, 813.1 ($M + Na^+$), 677.1 ($M + Na^+ - Cr(CO)_3$).

2-2′-Dimethoxy-3-η^6-(ethenylphenyltricarbonylchromium)-3′-formyl-1,1′-binaphthyl (15). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 10.60 (s, 1H, CHO), 8.63 (s, 1H, $H_{4'}$), 8.10 (d, *J* = *8*, 1H, $H_{6'}$), 8.02 (s, 1H, H_4), 7.83 (d, *J* = 8, 1H, H_6), 7.53−7.15 (m, 6H, H_7, H_8, H_9, $H_{7'}$, $H_{8'}$, $H_{9'}$), 7.03 (d, *J* = 12, 1H, H_{18}), 6.35 (d, *J* = 12, 1H, H_{17}), 5.44−5.30 (m, 5H, ArCr), 3.53 (s, 3H, OCH_3), 3.43 (s, 3H, $OCH_{3'}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 232.7 (CO−Cr), 190.5 (CHO), 156.4, 154.5 (C_2, $C_{2'}$), 137.0, 133.7, 130.2, 129.9, 129.5, 128.4, 125.8, 124.4 (C_1, C_3, C_5, C_{10}, $C_{1'}$, $C_{3'}$, $C_{5'}$, $C_{10'}$, $C_{14'}$), 131.8, 130.5, 130.4, 129.3, 128.8, 128.2, 127.9, 127.1, 125.9, 125.6, 125.4, 125.3 (C_4, C_6, C_7, C_8, C_9, C_{12}, C_{13}, $C_{4'}$, $C_{6'}$, $C_{7'}$, $C_{8'}$, $C_{9'}$), 105.3 (C_{14}), 93.5, 93.1, 92.1, 91.9, 91.6 (ArCr), 63.0, 61.4 (C_{11}, $C_{11'}$). IR (neat): ν (cm^{-1}) 1689 (CHO), 1877, 1960 (CO−Cr). UV (CH_3CN): λ 271 nm (ϵ 63 700 L mol^{-1} cm^{-1}). UV (CH_2Cl_2): λ 274 nm (ϵ 114 900 L mol^{-1} cm^{-1}). MS (MALDI-TOF, *m*/*z*): calcd for $C_{34}H_{24}CrO_6$, 580.1; found, 603.1 ($M + Na^+$), 467.1 ($M + Na^+ - Cr(CO)_3$).

2,2′-Dimethoxy-3-η^6-(ethenylphenyltricarbonylchromium)-3′-ethenylphenyl)-1,1′-binaphthyl (16). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.95 (s, 1H, H_4 or $H_{4'}$), 7.91 (s, 1H, H_4 or $H_{4'}$), 7.80 (d, *J*= *7*, 1H, H_6 or $H_{6'}$), 7.69 (d, *J*= *8*, 1H, H_6 or $H_{6'}$), 7.50−7.20 (m, 11H, H_7, H_8, H_9, $H_{7'}$, $H_{8'}$, $H_{9'}$, Ph), 7.04 (d, *J* = 12, 1H, H_{18}), 6.95 (d, *J* = 12, 1H, $H_{18'}$), 6.80 (d, *J* = 12, 1H, $H_{17'}$), 6.33 (d, *J* = 12, 1H, H_{17}), 5.50−5.20 (m, 5H, ArCr), 3.53 (s, 3H, OCH_3), 3.50 (s, 3H, $OCH_{3'}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 232.8 (CO−Cr), 154.7, 154.5 (C_2, $C_{2'}$), 137.0, 136.9, 134.0, 133.6, 133.4, 131.0, 130.4, 130.2, 129.5 (C_1, C_3, C_5, C_{10}, $C_{1'}$, $C_{3'}$, $C_{5'}$, $C_{10'}$, $C_{14'}$), 131.3, 131.1, 130.0, 129.9, 129.8, 129.1, 128.9, 128.3, 128.1, 128.0, 127.6, 127.3, 126.7, 126.3, 125.7, 125.1, 124.8 (C_4, C_6, C_7, C_8, C_9, C_{12}, C_{13}, $C_{4'}$, $C_{6'}$, $C_{7'}$, $C_{8'}$, $C_{9'}$, $C_{12'}$, $C_{13'}$, Ph), 105.6 (C_{14}), 93.5, 93.2, 92.2, 92.0, 91.6 (ArCr), 61.2, 61.1 (C_{11}, $C_{11'}$). IR (neat): ν (cm^{-1}) = 1888 (CO−Cr), 1964 (CO−Cr). MS (MALDI-TOF, *m*/*z*): calcd for $C_{41}H_{30}CrO_5$, 654.1; found, 677.3 ($M + Na^+$), 541.2 ($M + Na^+ - Cr(CO)_3$).

Synthesis of 2,2′-Dimethoxymethyl-3-η^6-(ethenylphenyltricarbonylchromium)-1,1′-binaphthyl (17). Under N_2, compound **13** (0.152 g, 0.27 mmol) prepared in a way similar to that described in the literature[18b] was dissolved in 15 mL of THF. ^{t}BuOK (*c* = 1.0 mol L^{-1} in THF, 0.324 mL, 0.324 mmol) was slowly added, and the mixture was stirred for 1 h at room temperature. Compound **2a** was then added at once to the orange solution of ylide, and the mixture was refluxed for 4 h. After being cooled at room temperature, the solution was hydrolyzed with 20 mL of an aqueous saturated ammonium chloride solution and extracted with dichloromethane (2 × 20 mL). The joined organic layers were washed with 20 mL of water, dried over anhydrous magnesium sulfate, filtered through Celite, and the solvent was evaporated under reduced pressure. The resulting yellow oil was purified by a silica gel chromatography column (15−40 μm, eluent EP/ethyl acetate: from 100/0 to 86/14 by portions of 50 mL and increment of 2%). Two compounds were separated corresponding to **17-Z** (66%, 0.109 g) and **17-E** (15%, 0.025 g), respectively, as a yellow and an orange solid.

Complex 17-Z. MS (FAB, *m*/*z*): calcd, 612.1; found, 612.1. ^{1}H NMR (200 MHz, $CDCl_3$): 2.86 (s, 3H, H_{20}), 3.22 (s, 3H, $H_{20'}$), 4.66 (d, *J* = 5.8 Hz, 1H, H_{19}), 4.76 (d, *J* = 5.8 Hz, 1H, H_{19}), 5.09 (d, *J* = 7.0 Hz, 1H, $H_{19'}$), 5.18 (d, *J* = 7.0 Hz, 1H, $H_{19'}$), 5.28−5.37 (m, 3H, H_{13}, H_{14}, H_{15}), 5.47 (d, *J* = 6.3 Hz, 2H, H_{12}, H_{16}), 6.36 (d, *J* = 12.2 Hz, 1H, H_{17} or H_{18}), 7.06 (d, *J* = 12.2 Hz, 1H, H_{18} or H_{17}), 7.21−7.45 (m, 6H, H_7, H_8, H_9, $H_{7'}$, $H_{8'}$, $H_{9'}$), 7.63 (d, *J* = 9.0 Hz, 1H, $H_{3'}$), 7.78 (d, *J* = 8.0 Hz, 1H, $H_{6'}$), 7.92 (s, 1H, H_4), 7.93 (d, *J* = 8.8 Hz, 1H, H_6), 8.02 (d, *J* = 8.8 Hz, 1H, $H_{4'}$). ^{13}C NMR (100 MHz, $CDCl_3$): 54.9 ($C_{20'}$), 55.7 (C_{20}), 90.4 (C_{14}), 91.3 (C_{13}), 92.3 (C_{11}), 92.5 (C_{12}), 94.0 ($C_{19'}$), 98.2 (C_{19}), 115.6 ($C_{3'}$), 123.2-124.2-124.5-124.9-125.3-126.5 (C_7, C_8, C_9, $C_{7'}$, $C_{8'}$, $C_{9'}$), 119.3 (C_3), 125.6-129.0-129.5-132.7-132.8 (C_1, C_5, C_{10}, $C_{1'}$, $C_{5'}$, $C_{10'}$), 125.7 (C_{17} or C_{18}), 126.9 (C_6, $C_{6'}$), 128.6 (C_{17} or C_{18}), 129.0 (C_4, $C_{4'}$), 150.8 (C_2), 151.8 ($C_{2'}$), 233.3 (C_{21}, C_{22}, C_{23}). IR (neat): ν (cm^{-1}) 1621 (C═C), 1880, 1962 (CO). UV−visible ($CHCl_3$) λ 267 (ϵ = 22 867 L mol^{-1} cm^{-1}), λ 330 (ϵ = 978 L mol^{-1} cm^{-1}); (CH_2Cl_2) λ 265 (ϵ = 32 533 L mol^{-1} cm^{-1}); (CH_3CN) λ 313 (ϵ = 23 602 L mol^{-1} cm^{-1}); λ 386 (ϵ = 4073 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{35}H_{28}CrO_7$: C, 68.61; H, 4.61. Found: C, 68.50; H, 4.49. MS (FAB *m*/*z*): calcd for $C_{35}H_{28}CrO_7$, 612.1; found, 612.1 (M^+).

Complex 17-E. ^{1}H NMR (400 MHz, $CDCl_3$): 2.83 (s, 3H, H_{20}), 3.20 (s, 3H, $H_{20'}$), 4.65 (d, *J* = 5.6 Hz, 1H, H_{19}), 4.71 (d, *J* = 5.6 Hz, 1H, H_{19}), 5.07 (d, *J* = 6.9 Hz, 1H, $H_{19'}$), 5.19 (d, *J* = 6.9 Hz, 1H, $H_{19'}$), 5.36 (t, *J* = 6.2 Hz, 1H, H_{14}), 5.50 (t, *J* = 6.2 Hz, 2H, H_{13}), 5.67 (d, *J* = 6.2 Hz, 2H, H_{12}), 6.93 (d, *J* = 16.2 Hz, 1H, H_{17} or H_{18}), 7.19−7.49 (m, 6H, H_7, H_8, H_9, $H_{7'}$, $H_{8'}$, $H_{9'}$), 7.60 (d, *J* = 5.7 Hz, 1H, $H_{3'}$), 7.92 (d, *J* = 6.0 Hz, 1H, $H_{6'}$), 7.93 (d, *J* = 8.8 Hz, 1H, H_6), 8.01 (d, *J* = 5.7 Hz, 1H, $H_{4'}$), 8.23 (s, 1H, H_4). ^{13}C NMR (50 MHz, $CDCl_3$): 55.0 (C_{20}), 55.7 ($C_{20'}$), 89.8 (C_{14}), 90.3 (C_{13}), 91.7 (C_{11}), 94.0 (C_{12}), 98.2 ($C_{19'}$), 105.1 (C_{19}), 115.6 ($C_{3'}$), 123.2-123.4-124.4-124.9-125.7-126.8 (C_7, C_8, C_9, $C_{7'}$, $C_{8'}$, $C_{9'}$), 119.6 (C_3), 125.6-128.9-130.4-132.9-136.7 (C_1, C_5, C_{10}, $C_{1'}$, $C_{5'}$, $C_{10'}$), 125.7 (C_{17} or C_{18}), 126.7 (C_6, $C_{6'}$), 128.8 (C_{17} or C_{18}), 129.5 (C_4, $C_{4'}$), 150.3 (C_2), 151.9 ($C_{2'}$), 231.9 (C_{21}, C_{22}, C_{23}). IR (neat): 1652 C═C, 1887, 1962 (CO). UV−visible ($CHCl_3$) λ 264 (ϵ = 21 692 L mol^{-1} cm^{-1}); (CH_2Cl_2) λ 290 (ϵ = 44 281 L mol^{-1} cm^{-1}), λ 427 (ϵ = 792 L mol^{-1} cm^{-1}); (CH_3CN) λ 266 (ϵ = 28 234 L mol^{-1} cm^{-1}), λ 309 (ϵ = 20 064 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{35}H_{28}CrO_7$: C, 68.61; H, 4.61. Found: C, 68.42; H, 4.43. MS (FAB *m*/*z*): calcd for $C_{35}H_{28}CrO_7$, 612.1; found, 612.1 (M^+).

Synthesis of Ferrocenylmethanol.[22] A solution of ferrocenecarboxaldehyde (1.07 g, 5.0 mmol) in methanol (50 mL) was cooled at 0 °C. $NaBH_4$ (0.95 g, 25 mmol) dissolved in an aqueous solution of sodium hydroxide (2 N) was then added via a canula, and the resulting mixture was stirred and allowed to warm to room temperature overnight. The methanol was evaporated with vigorous stirring, and the resulting aqueous solution was extracted with diethyl ether (3 × 30 mL). The organic layer was washed with water (2 × 30 mL), dried over anhydrous $MgSO_4$, filtered through Celite, and evaporated under reduced pressure. The treatment led to the ferrocenylmethanol in quantitative yield. ^{1}H NMR (200 MHz, $CDCl_3$): 1.65 (t, *J* = 6.1 Hz, 1H, OH), 4.24 (s, 7H, C_5H_5 and C_5H_4), 4.29 (m, 2H, C_5H_4), 4.37 (d, *J* = 6.1 Hz, 2H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): 61.2 (C_5H_4), 68.4−68.9 (C_5H_4), 68.7 (C_5H_5), 88.7 (CH_2).

Synthesis of (Ferrocenylmethyl)triphenylphosphonium Bromide (18).[22] Ferrocenylmethanol (0.432 g, 2.0 mmol) was dissolved in CH_2Cl_2 (10 mL) with triphenylphosphonium hydrobromide, PPh_3·HBr[18b] (0.618 g, 1.8 mmol), in the presence of activated molecular sieve (4 Å). The solution was refluxed during 1 h. After being cooled at room temperature, the mixture was filtered under N_2 and dry diethyl ether was added until persistence of a yellow precipitate. After decanting, the liquid layer was removed with a syringe, and the solid was washed twice with dry diethyl ether (10 mL). The (ferrocenylmethyl)triphenylphosphonium bromide, **18**, was obtained in 80% yield (0.779 g). For $C_{29}H_{26}BrFeP$ *M* = 541. ^{1}H NMR (400 MHz, $CDCl_3$): 3.94 (sb, 2H, C_5H_4), 4.02 (sb, 2H, C_5H_4), 4.33 (s, 5H, C_5H_5), 5.05 (d, *J* = 11.7 Hz, 2H, CH_2), 7.60−7.73 (m, 15H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): 31.3 (d, *J* =

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48 Hz, CH_2), 69.2−71.0 (C_5H_4), 70.4 (C_5H_5), 70.9 (d, J = 2 Hz, C_5H_4), 118.5 (d, J = 85 Hz, C_{Ph}−P^+), 130.5 (d, J = 12.0 Hz, C_{Ph}−P^+), 134.7 (d, J = 10 Hz, $C_{Ph-}P^+$), 135.3 (d, J = 3.5 Hz, C_{Ph}−P^+). Anal. Calcd for $C_{29}H_{26}PFeBr$: C, 61.10; H, 5.60. Found: C, 61.18; H, 5.51. MS (MALDI-TOF, *m*/*z*): calcd for C^+, 461; found, 461 C^+ (M − Br), 1002 (M + 1 + C^+).

Synthesis of 2,2′-Dimethoxymethyl-3-ferrocenylethenyl-1,1′-binaphthyl (19-E and -Z). (Ferrocenylmethyl) triphenylphosphonium bromide,[18a] **18** (0.171 g, 0.50 mmol), was dissolved under N_2 in THF (15 mL). The solution was cooled at 0 °C, and a solution of ^{t}BuOK in THF (c = 1.0 mol L^{-1}, 0.60 mL, 0.60 mmol) was slowly added. The mixture was stirred at 0 °C for 1 h. In another flask, compound **2a** (0.201 g, 0.50 mmol) was dissolved in THF (10 mL). The suspension was cooled at −78 °C. The red solution of ylide was then cooled at the same temperature, and the suspension of **2a** was added via a canula. The resulting mixture was stirred at −40 °C. After 2 h, the solution was hydrolyzed with 20 mL of an aqueous saturated ammonium chloride solution at room temperature and extracted twice with 20 mL of dichloromethane. The joined organic phases were washed with 20 mL of water, dried over anhydrous magnesium sulfate, filtered through Celite, and the solvents evaporated under reduced pressure. The residue was purified by silica gel chromatography column (15−40 μm, eluent EP/Et_2O: from 100/0 to 90/10 by portions of 50 mL and increment of 2%). A mixture of red complexes **19-Z** and **19-E** that could not be separated by silica gel chromatography column was obtained in 45% yield, 132 mg (*Z*/*E*: 3/1, NMR ratio). IR (neat): ν (cm^{-1}) 1624 (C═C: $C_{17-}C_{18}$). MS (FAB *m*/*z*): calcd for $C_{36}H_{32}FeO_4$, 584.2; found, 584.2 (M^+). Anal. Calcd for $C_{36}H_{32}FeO_4$: C, 73.95; H, 5.52. Found: C, 74.14; H, 5.61.

19-Z. ^{1}H NMR (400 MHz, $CDCl_3$): 2.53 (s, 3H, H_{20}), 2.98 (s, 3H, $H_{20'}$), 4.04 (s, 5H, Cp), 4.13 (m, 2H, H_{12} and H_{15} or H_{13} and H_{14}), 4.19 (m, 2H, H_{13} and H_{14} or H_{12} and H_{15}), 4.65 (d, J = 5.7 Hz, 1H, H_{19}), 4.71 (d, J = 5.7 Hz, 1H, H_{19}), 4.94 (d, J = 6.8 Hz, 1H, $H_{19'}$), 5.07 (d, J = 6.8 Hz, 1H, $H_{19'}$), 6.40 (d, J = 11.9 Hz, 1H, H_{17} or H_{18}), 6.62 (d, J = 11.8 Hz, 1H, H_{18} or H_{17}), 7.07−7.29 (m, 6H, H_7, H_8, H_9, $H_{7'}$, $H_{8'}$, $H_{9'}$), 7.50 (d, J = 9.1 Hz, 1H, $H_{3'}$), 7.69 (d, J = 8.3 Hz, 1H, $H_{6'}$), 7.78 (d, J = 8.1 Hz, 1H, H_6), 7.87 (d, J = 9.1 Hz, 1H, $H_{4'}$), 7.93 (s, 1H, H_4). ^{13}C NMR (50 MHz, $CDCl_3$): 55.9 (C_{20}), 56.2 ($C_{20'}$), 69.3 (C_{16}), 69.4−69.7 ($C_{12-}C_{15}$ and $C_{13-}C_{14}$), 95.1 ($C_{19'}$), 98.8 (C_{19}), 116.9 ($C_{3'}$), 121.5-124.1-124.9-125.7-125.9-129.5-130.7-131.3-131.1-132.1-133.0-133.3-134.1 -134.2 (C_1, C_3, C_5, C_7, C_8, C_9, C_{10}, C_{11}, $C_{1'}$, $C_{5'}$, $C_{7'}$, $C_{8'}$, $C_{9'}$, $C_{10'}$), 123.5 (C_{17} or C_{18}), 127.8 (C_6), 127.9 ($C_{6'}$), 129.4 (C_{18} or C_{17}), 129.6 (C_4), 129.8 ($C_{4'}$), 151.9 (C_2), 152.9 ($C_{2'}$). **19-E.** ^{1}H NMR (400 MHz, $CDCl_3$): 2.68 (s, 3H, H_{20}), 2.98 (s, 3H, $H_{20'}$), 4.08 (m, 2H, H_{12} and H_{15} or H_{13} and H_{14}), 4.10 (s, 5H, H_{16}), 4.10 (m, 2H, H_{12} and H_{15} or H_{13} and H_{14}), 4.57 (d, J = 5.7 Hz, 1H, H_{19}), 4.62 (d, J = 5.7 Hz, 1H, H_{19}), 4.93 (d, J = 6.8 Hz, 1H, $H_{19'}$), 5.07 (d, J = 6.8 Hz, 1H, $H_{19'}$), 7.05 (d, J = 15.9 Hz, 1H, H_{17} or H_{18}), 7.07−7.29 (m, 6H, H_7, H_8, H_9, $H_{7'}$, $H_{8'}$, $H_{9'}$), 7.51 (d, J = 9.1 Hz, 1H, $H_{3'}$), 7.69 (d, J = 8.3 Hz, 1H, $H_{6'}$), 7.82 (d, J = 8.1 Hz, 1H, H_6), 7.88 (d, J = 9.1 Hz, 1H, $H_{4'}$), 8.08 (s, 1H, H_4). ^{13}C NMR (50 MHz, $CDCl_3$): 55.9 (C_{20}), 56.7 ($C_{20'}$), 68.9 ($C_{12-}C_{15}$ and $C_{13-}C_{14}$), 69.3 (C_{16}, $C_{12-}C_{15}$ and $C_{13-}C_{14}$), 95.0 ($C_{19'}$), 99.1 (C_{19}), 116.8 ($C_{3'}$), 121.5-124.1-124.9-125.7-125.9-129.5-130.7-131.3-131.1-132.1-133.0-133.3-134.1-134.2 (C_1, C_3, C_5, C_7, C_8, C_9, C_{10}, C_{11}, $C_{1'}$, $C_{5'}$, $C_{7'}$, $C_{8'}$, $C_{9'}$, $C_{10'}$), 121.3 (C_{17} or C_{18}), 127.8 (C_6), 127.9 ($C_{6'}$), 128.9 (C_{17} or C_{18}), 129.7 (C_4, $C_{4'}$), 151.1 (C_2), 152.9 ($C_{2'}$).

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Supporting Information Available: Tables of crystal data, atomic coordinates, and bond distances and angles for complexes **8a** and **17Z**. Crystallographic data as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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