Tunable π-Interactions in Monomeric Organozinc Complexes: Solution and Solid-State Studies

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A series of the calix[4]arene ligands, partially oxygen-depleted at the 1 and 3 positions via the Sonogashira cross-coupling reaction with several arylacetylenes, were prepared. Upon reaction with R_2Zn (R = Me, Et, C_6F_5), the corresponding organozinc complexes were obtained. X-ray analysis showed weak π-interactions between the organozinc fragment and the triple bonds. In addition, the solution ^{13}C NMR studies showed good correlation between the strength of these interactions and electron density at the acetylene group, with more electron-rich alkynes binding stronger to the Zn center. The latter was also supported by DFT calculations on a model compound. These results show that, albeit weak, π-interactions of organozinc compounds can be observed and fine-tuned in both solution and the solid state.

Introduction

Organozinc reagents are widely utilized in modern synthetic organic chemistry, particularly in asymmetric catalysis.[1] In many cases, organic transformations assisted by organozincs involve substrates bearing alkene or alkyne functions.[2] While unsaturated substrates usually show strong π-interactions with the majority of electron-rich d^{10} complexes,[3] such interactions are noticeably scarce in the isoelectronic electron-rich zinc(II) complexes. Since the Zn−alkene or Zn−alkyne interaction virtually lacks the back-bonding component,[4,5] these complexes should be considerably weaker for zinc compared with other d^{10} metals. It is, nevertheless, important to keep in mind that zinc does not use its d-electrons for binding and often is not considered a transition metal.

Zinc alkene complexation was very recently reported to exist in divinyl zinc derivatives in the solid state but not in solution.[6] Recrystallization of bis(perfluoroaryl)zinc complexes from toluene gave crystalline compounds that showed Zn π-interactions with the toluene molecule.[7a] However, the solution ^1H and ^{13}C NMR spectra of these complexes[7a,b] exhibit signals expected for the noncoordinated toluene.[8] No benzene incorporation into the crystal structure was observed when bis(pentafluorophenyl)zinc was crystallized from benzene.[9]

Circumstantial evidence for the Zn π-interactions was obtained from the solution NMR studies of di-4-hexynyl- and di-4-pentenylzinc; however, these earlier reports were not verified by the X-ray crystallography.[10,11] Although alkene coordination to Zn appears to be responsible for the stereoselectivity of allylzincation and zinc-assisted cyclopropanation reactions,[12] formation of a π-complex between allylzinc bromide and ethylene was calculated to be slightly endothermic,[13] emphasizing the delicate balance in assessment of Zn π-interactions in solution and the solid state. Thus far, π-interactions in *monomeric* complexes have been confirmed only for the Lewis acidic zinc dihalides.[14] In this paper, we report the first solution and X-ray studies on the fine-tuning of the organozinc π-interactions with an alkyne ligand.

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(1) von Wangelin, A. J.; Frederiksen, M. U. Zinc-mediated reactions. In *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*, 2nd ed.; Beller, M., Bolm, C., Eds.; Wiley-VCH: New York, 2004; p 519.

(2) For the latest references see: (a) Lorthiois, E.; Meyer, C. Cabozincation of alkenes and alkynes. In *The Chemistry of Organozinc Compounds*; Rappoport, Z., Marek, I., Eds.; Wiley-VCH: New York, 2006; Chapter 19, p 863. (b) Reiser, O. *Angew. Chem., Int. Ed*. **2006**, *45*, 2838. (c) Pu, L. *Tetrahedron* **2003**, *59*, 9873.

(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Sausalito, CA, 1987.

(4) This lack of back-donation is attributed to the large orbital promotion energy: Elschenbroich, C.; Salzer, A. *Organometallics: A Concise Introduction*, 2nd ed.; VCH Publishers Inc.: New York, 1992; p 256.

(5) (a) For relevant discussion see: Lin, J.; Jones, P.; Guckert, J.; Solomon, E. I. *J. Am. Chem. Soc*. **1991**, *113*, 8312. (b) Hg(II) alkyne complexes, also lacking the back-bonding component, have been reported: Faville, S. J.; Henderson, W.; Mathieson, T. J.; Nicholson, B. K. *J. Organomet. Chem*. **1999**, *580*, 363.

(6) Wooten, A.; Carroll, P. J.; Maestri, A. G.; Walsh, P. J. *J. Am. Chem. Soc*. **2006**, *128*, 4624.

(7) (a) Guerrero, A.; Martin, E.; Hughes, D. L.; Kaltsoyannis, N.; Bochmann, M. *Organometallics* **2006**, *25*, 3311. (b) Walker, D. A.; Woodman, T. J.; Hughes, D. L.; Bochmann, M. *Organometallics* **2001**, *20*, 3772.

(8) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem*. **1997**, *62*, 7512.

(9) Sun, Y.; Piers, W. E.; Parvez, M. *Can. J. Chem.* **1998**, *76*, 513.

(10) Alkyne complexes: (a) Okninska, E.; Starowieyski, K. B. *J. Organomet. Chem*. **1989**, *376*, 7. (b) Okninska, E.; Starowieyski, K. B. *J. Organomet. Chem.* **1988**, *347*, 1.

(11) Alkene complexes: (a) Albright, M. J.; St. Denis, J. N.; Oliver, J. P. *J. Organomet. Chem.* **1977**, *125*, 1. (b) St Denis, J.; Oliver, J. P.; Dolzine, T. W.; Smart, J. B. *J. Organomet. Chem.* **1974**, *71*, 315.

(12) (a) Marek, I.; Beruben, D.; Normant, J.-F. *Tetrahedron Lett.* **1995**, *36*, 3695. (b) Beruben, D.; Marek, I.; Normant, J.-F.; Platzer, N. *J. Org. Chem*. **1995**, *60*, 2488.

(13) (a) Marek, I.; Schreiner, P. R.; Normant, J. F. *Org. Lett.* **1999**, *1*, 929. (b) See also: Hirai, A.; Nakamura, M.; Nakamura, E. *J. Am. Chem. Soc*. **2000**, *122*, 11791.

(14) (a) Lang, H.; Mansilla, N.; Rheinwald, G. *Organometallics* **2001**, *20*, 1592. (b) Enders, M.; Ludwig, G.; Pritzkow, H. *Eur. J. Inorg. Chem*. **2002**, 539.

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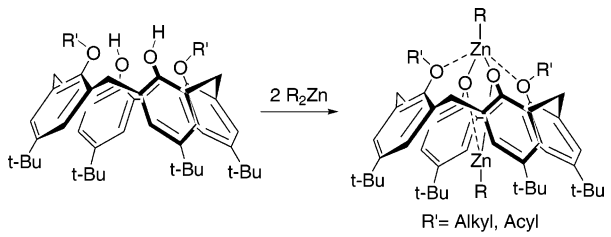
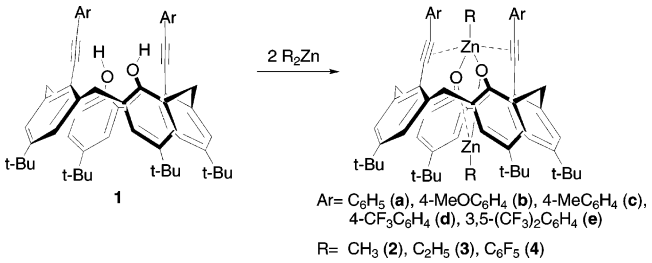
Scheme 1



Scheme 2



Results and Discussion

We recently showed that the reaction of 2 equiv of a dialkylzinc reagent with 1,3-diethers or diesters of calix[4]arene (calixarene) results in the bimetallic inclusion complexes where one of the alkylzinc groups is located inside the calixarene cavity. This internal zinc center is coordinated to two of the oxygen atoms, while the second one remains on top of the calixarene phenolic rim and coordinated to all four oxygen atoms (Scheme 1).[15] As a continuation of this work, we reacted Me_2-Zn with the calixarene ligand **1a**, where two of the oxygen atoms have been replaced with a phenylacetylene unit.[16] The ^{1}H NMR spectrum of the reaction mixture indicated the quantitative formation of the new bimetallic complex **2a**, similar to that previously reported, showing that the formation of these complexes is not affected by the absence of the two oxygen donors (Scheme 2).

To verify the composition of **2a**, we performed crystallographic studies of its crystal. The X-ray structure of **2a** (Figure 1) shows that the general characteristics of this complex are similar to the complexes with more common calixarene ligands.[15] An important feature of this structure is the relatively short distances, shorter than the sum of the van der Waals radii (3.09 Å), between the external zinc atom and carbon atoms of one of the triple bonds of the calixarene ligand, 2.7695(37) and 3.0667(37) Å. There is also a noticeable difference between the C3−Zn1−O2 and C3−Zn1−O1 bond angles, 148.48° and 133.25°, respectively, a feature not observed in other Zn calixarene complexes.[15] Although the interactions between the zinc center and second triple bond are less apparent if only Zn−carbon distances (2.9545(34) and 3.3661(36) Å) are counted, the solution ^{1}H and ^{13}C NMR spectra show symmetrical patterns even at −80 °C without preferential Zn coordination to either of the triple bonds. The NMR data suggest that, in solution, the zinc center either is equally interacting with both alkyne groups in a five-coordinate fashion or exists in a very fast equilibrium even at low temperatures.

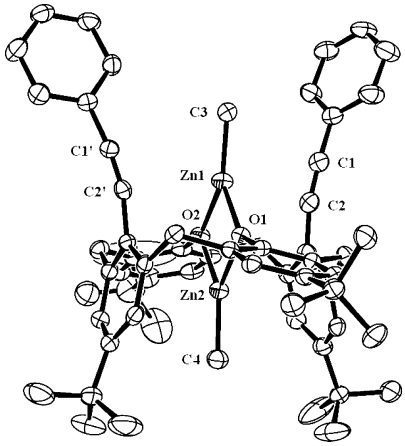


Figure 1. ORTEP structures (50% probability) of molecules of **2a**. Hydrogen atoms and solvent (pentane) molecule are omitted for clarity. Labels C1 and C1′, and C2 and C2′, are used to allow better comparison between the alkyne ligands on each side. The corresponding atoms are not symmetry related. Selected distances (Å) and angles (deg): Zn1−O1 1.971(2), Zn1−O2 1.992(2), Zn1−C1 3.0667(37), Zn1−C2 2.7695(37), Zn1−C1′ 3.3661(36), Zn1−C2′ 2.9545(34), Zn1−Zn2 3.067, Zn1−C3 1.941(4), Zn2−C4 1.940(4); C3−Zn1−O2 148.48(13), C3−Zn1−O1 133.25(13), O1−Zn1−O2 78.19(9).

To investigate the alkyne π-interactions in the organozinc calixarene complexes, we prepared a series of ligands **1b**−**e** with different substituents in the aromatic ring of the alkyne part of the molecule. Upon the reaction with Me_2Zn, complexes **2b**−**e** were obtained in quantitative yields (Scheme 2). Interestingly, the ^{13}C NMR $\Delta\delta$ of the triple-bond carbon atoms' chemical shifts between the complexes and free ligands shows very good correlation with the σ_p-Hammett parameters of the substituents in the aromatic ring (Figure 2).[17] In all cases, the signals of the carbon atoms of the triple bond are shifted *downfield*, suggesting some weakening of the triple bond (Table 1). These shifts were more significant for the complexes bearing electron-donating groups, implying stronger interactions of the electron-rich alkynes with the zinc center.

A similar trend was observed for the ^{13}C NMR signal of the zinc-bound methyl group, which showed steady upfield shifts for complexes with more electron-rich alkyne ligands. To ensure that this trend is not a result of the direct interaction of the aromatic ring with the methyl group, we prepared the corresponding ethylzinc complexes (**3**, Scheme 2). The ^{13}C NMR analysis showed that the Zn-bound *methylene* group of the ethyl ligand is more affected by the electronic properties of the substituent in the aromatic ring than the corresponding methyl end group. Due to its closer proximity, this group would be more susceptible to the aromatic ring-current effects should the latter be influencing the chemical shifts of the alkylzinc groups. Interestingly, the triple-bond carbon atoms show weaker interactions with the more electron-rich ethylzinc fragment in **3** than with the methylzinc fragment in **2**, as confirmed by the ^{13}C NMR $\Delta\delta$ analysis (Table 2). We also prepared complexes **4**, containing pentafluorophenyl groups (Scheme 2), significantly weaker donors than alkyls, at the Zn center. The ^{13}C NMR analysis showed that the triple bonds in **4** exhibit larger chemical shifts versus the free ligands than in **2**. Again, electron-donating substituents in the aromatic ring resulted in stronger Zn−triple bond π-interactions (Table 3). Favorable π-stacking interactions between the electron-rich aromatic groups and pentafluorophe-

(15) (a) Bukhaltsev, E.; Goldberg, I.; Vigalok, A. *Organometallics* **2004**, *23*, 4540. (b) Bukhaltsev, E.; Goldberg, I.; Vigalok, A. *Organometallics* **2005**, *24*, 5732.

(16) (a) Al-Saraierh, H.; Miller, D. O.; Georghiou, P. E. *J. Org. Chem.* **2005**, *70*, 8273. (b) We modified the original protocols by using a more reactive *t*-Bu_3P/Pd(dba)$_2$ cross-coupling catalyst. See Experimental Part for details.

(17) Hansch, C. A.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

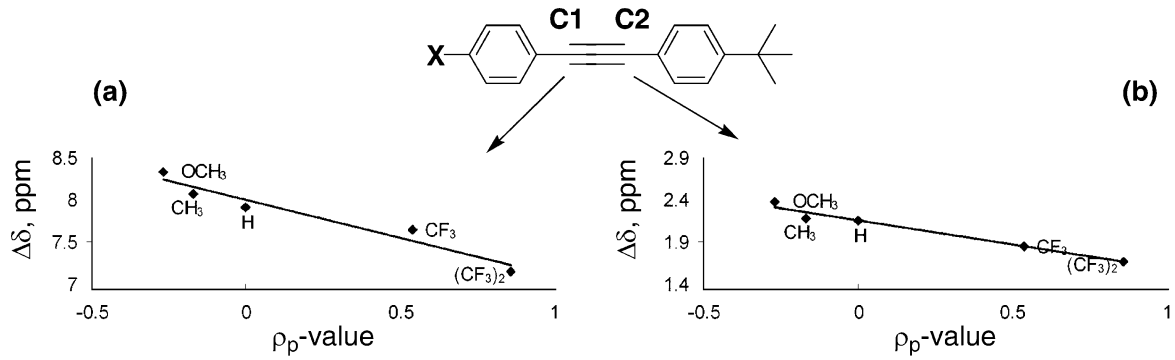


Figure 2. Difference in chemical shifts ($\Delta\delta$, ppm) of the triple-bond carbons C1 (a) and C2 (b) in complexes **2** versus free ligands as a function of the Hammett ρ_{para} values.[17] For **2e**, twice the value of ρ_{meta} was taken.

Table 1. ^{13}C NMR Chemical Shifts of the Triple-Bond Carbons in Complexes 2a−e and 6 versus the Corresponding Ligands

		δ C≡C ^{13}C NMR,[b] ppm		ligand δ C≡C ^{13}C NMR, ppm		$\Delta\delta$, ppm	
compound	σ_{para}[a]	C1	C2	C1	C2	C1	C2
2b	−0.27	106.59	89.10	98.26	86.73	8.33	2.37
2c	−0.17	106.43	89.57	98.37	87.40	8.06	2.17
2a	0.00	106.05	90.10	98.14	87.95	7.91	2.15
2d	0.54	104.16	92.17	96.51	90.32	7.65	1.85
2e[c]	0.86[c]	101.96	93.01	94.81	91.35	7.15	1.66
6	−0.27	107.32	88.94	98.52	86.55	8.80	2.39
	0.54	103.58	92.42	96.28	90.63	7.30	1.79

[a] Taken from ref 17. [b] All spectra were observed in C_6D_6 at 22 °C. [c] For **2e**, twice the value of ρ_{meta} was taken.

Table 2. ^{13}C NMR Chemical Shifts of the Triple-Bond Carbons in Complexes 3a−e versus the Corresponding Ligands

		δ C≡C ^{13}C NMR, ppm		ligand δ C≡C ^{13}C NMR, ppm		$\Delta\delta$, ppm	
compound	σ_{para}	C1	C2	C1	C2	C1	C2
3b	−0.27	106.06	88.59	98.26	86.73	7.80	1.86
3c	−0.17	105.91	89.09	98.37	87.40	7.54	1.69
3a	0.00	105.54	89.60	98.14	87.95	7.40	1.65
3d	0.54	103.67	91.66	96.51	90.32	7.17	1.34
3e	0.86[c]	101.51	92.54	94.81	91.35	6.70	1.19

Table 3. ^{13}C NMR Chemical Shifts of the Triple-Bond Carbons in Complexes 4a−d versus the Corresponding Ligands

		δ C≡C ^{13}C NMR, ppm		ligand δ C≡C ^{13}C NMR, ppm		$\Delta\delta$, ppm	
compound	σ_{para}	C1	C2	C1	C2	C1	C2
4b	−0.27	108.67	88.32	98.26	86.73	10.41	1.59
4c	−0.17	108.30	88.72	98.37	87.40	9.93	1.32
4a	0.00	107.84	89.12	98.14	87.95	9.70	1.17
4d	0.54	105.65	90.85	96.51	90.32	9.15	0.53

nylzinc moiety may also contribute to the observed large chemical shifts.

To further verify the tunability of the Zn−alkyne interactions, we synthesized the calixarene dialkyne ligand **5**, bearing different alkyne groups at the opposite sides of the calixarene cone. Upon reacting with 2 equiv of Me_2Zn, this compound afforded the expected bimetallic zinc complex **6** (Scheme 3). Interestingly, comparison of the $\Delta\delta$ of the ^{13}C NMR triple-bond signals in **6** versus **5** with the corresponding value for **2b** and **2d** (versus **1b** and **1d**, respectively) showed that the Zn π-interactions are stronger for the electron-rich alkyne part of the ligand and weaker for the electron-poor alkyne group (Table 1). This unsymmetrical binding was confirmed by the X-ray analysis of complex **6** (Figure 3), which shows that the distances between the "electron-rich" alkyne carbons and zinc atom are approximately 0.05 Å shorter than the corresponding distances involving the "electron-poor" part of the molecule (2.8706(38) versus 2.9222(39) Å for C2 and 3.1152(39) versus 3.1719(42) Å for C1). Unlike in **2a**, the arylalkyne units in **6** are aligned parallel to each other.[18]

The coordination modes of the Zn−alkyne complexes were further validated by computational methods using the Gaussian03 program package.[19] DFT calculations at the PBE0/SDD level of theory[20−22] of **6a** (the simplified analogue of **6** where the *t*-Bu groups have been replaced by hydrogen atoms) provided structural features closely resembling those observed in the X-ray analysis of **6**. In particular, the calculations show that the external zinc center is located closer to the electron-rich alkyne, with Zn−C2 and Zn1−C1 distances of 2.841 and

(18) We observed a similar alignment in the X-ray structure of **2b**. Although there are severe disorders in this structure at the "periphery" of the molecule (OMe and *t*-Bu groups), the central part of the molecule in the proximity of the Zn atoms was solved reliably. In addition to the parallel positioning of the aryl groups, the crystal structure of **2b** shows average Zn−C2 and Zn−C1 distances of 2.879 and 3.092 Å, respectively, which is similar to what was observed for the zinc interactions with the electron-rich part of the molecule of **6**.

(19) Frisch, M. J. et al. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(20) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(21) Dunning, T. H., Jr.; Hay, P. J. *Modern Theoretical Chemistry*; Plenum: New York, 1976; Vol. 3, p 1.

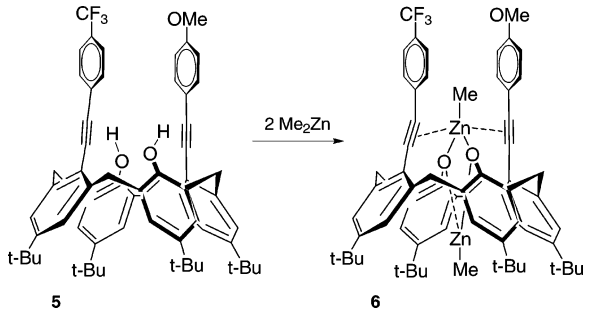
(22) Dolg, M. Effective Core Potentials. In *Modern Methods and Algorithms of Quantum Chemistry*; John von Neumann Institute for Computing: Jülich, 2000; Vol. 1, p 479.

Table 4. Crystal Structure Information for Complexes 2a and 6

	2a	6
empirical formula	$C_{62}H_{68}O_2Zn_2 \cdot C_5H_{12}$	$C_{64}H_{69}F_3O_3Zn_2$
fw	1048.05	1073.93
tempe (K)	110(2)	110(2)
wavelength (Å)	0.71073	0.71073
radiation type	Mo Kα	Mo Kα
cryst syst	monoclinic	triclinic
space group	$P2/c$	$P\bar{1}$
unit cell dimens		
a (Å)	23.3100(3)	10.2094(4)
b (Å)	12.3369(2)	14.1816(4)
c (Å)	20.4060(5)	19.7097(7)
α (deg)	90.00	104.3222(12)
β (deg)	105.4498(6)	98.4218(17)
γ (deg)	90.00	96.127(3)
cell volume (Å^3)	5656.16(18)	2704.58(16)
Z	4	2
calcd density (g m^{-3})	1.231	1.319
cryst descrip	colorless plates	colorless prisms
crystal size (nm)	0.50 × 0.30 × 0.10	0.30 × 0.25 × 0.25
θ range for data collection (deg)	2.26 to 27.51	1.41 to 28.28
index ranges	$-28 \le h \le 27$ $-15 \le k \le 0$ $0 \le l \le 15$	$0 \le h \le 12$ $-17 \le k \le 17$ $-24 \le l \le 23$
no. of reflns collected/ unique	10 967/7889	10 498/7856
refinement method	full-matrix F^2	full-matrix F^2
goodness-of-fit	1.012	1.044
no. of data/restrains/ params	10 967/1/628	10 498/0/658
$R_1(I > 2\sigma(I))$	0.0552	0.0624
wR_2(all data)	0.1382[a]	0.1620[b]

[a] $w = 1/[\sigma^2(F_o^2) + (0.0807P)^2 + 6.7515P]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] $w = 1/[\sigma^2(F_o^2) + (0.0967P)^2 + 3.4491P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Scheme 3



3.144 Å, respectively. Interestingly, the calculations also show a slight tilt of the methyl group toward the electron-poor alkyne (Zn2−Zn1−C3 angle of 172.5° versus 176.4° in the experimental structure), suggesting that there is some tendency of the Zn1 center to be in a tetrahedral configuration with C3, O1, O2, and the electron-donating alkyne moiety as ligands.

In conclusion, we showed that the organozinc π-interactions can be directly tuned and observed in both solution and the solid state. As no back-bonding has been shown for zinc, more electron-rich alkynes form stronger bonds to the metal center. Although the interactions are generally weak, our observations support the notion that π-interactions with organozinc reagents exist in solution and, thus, can influence their reactivity in catalytic transformations.

Experimental Part

General Information. All operations with air- and moisture-sensitive compounds were performed in a nitrogen-filled Innovative Technology glovebox. All solvents were degassed and stored under high-purity nitrogen over activated 4 Å molecular sieves. All deuterated solvents were stored under high-purity nitrogen over 3 Å molecular sieves. Commercially available reagents were purchased from Aldrich and used as received. The NMR spectra were recorded on Bruker AC 200 MHz and Bruker AMX 400 MHz spectrometers. ^{1}H and ^{13}C NMR signals are reported in ppm downfield from TMS. ^{1}H signals are referenced to the residual proton of a deuterated solvent (7.26 ppm for $CDCl_3$, 7.15 ppm for C_6D_6). For ^{13}C NMR spectra, the following signals were used as a reference: 77.36 ppm for $CDCl_3$, 128.62 ppm for C_6D_6. ^{19}F chemical shifts are reported in ppm downfield from $CClF_3$. All $\Delta\delta$ ^{13}C{^{1}H} NMR measurements were performed at 22 °C in C_6D_6 unless stated otherwise. Elemental analyses were performed in the laboratory for microanalysis at the Hebrew University of Jerusalem. The high-resolution mass spectra were recorded at the Maiman Institute for Proteome Research at Tel Aviv University.

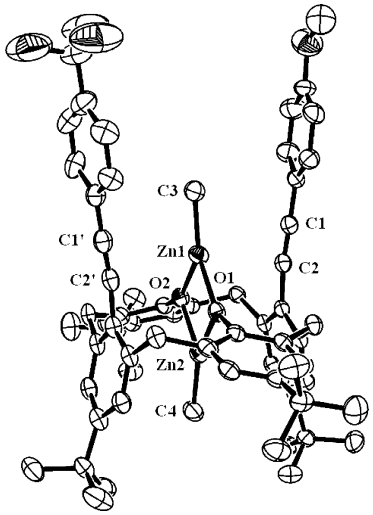


Figure 3. ORTEP structures (50% probability) of molecules of **6**. Hydrogen atoms are omitted for clarity. Labels C1 and C1′, and C2 and C2′, are used to allow better comparison between the alkyne ligands on each side. The corresponding atoms are not symmetry related. Selected distances (Å) and angles (deg): Zn1−O1 2.006(3), Zn1−O2 1.973(3), Zn1−C1 3.1152(39), Zn1−C2 2.8706(38), Zn1−C1′ 3.1719(42), Zn1−C2′ 2.9222(39), Zn1−Zn2 3.0517, Zn1−C3 1.944(5), Zn2−C4 1.929(5); C3−Zn1−O2 137.70(19), C3−Zn1−O1 143.38(19), O1−Zn1−O2 78.72(11).

General Procedure for the Preparation of Ligands 1a−e. All reactions were carried out under an inert atmosphere of pure nitrogen using 10 mol % of a Pd catalyst, 250 mol % of CuI, 4 equiv of DBU, and 3 equiv of acetylene. A typical procedure is reported below.

1a. To a mixture of P(*t*-Bu)$_3$H$^+$BF$_4^-$ (16 mg, 0.055 mmol) and Pd_2dba_3 (12.5 mg, 0.014 mmol) dissolved in 10 mL of dry DMF were added CuI (250 mg, 1.31 mmol), DBU (334 mg, 2.20 mmol), phenylacetylene (169 mg, 1.65 mmol), and bis(OTf)-*p*-*tert*-butylcalix[4]arene (500 mg, 0.55 mmol), and the mixture was heated at 100 °C for 4 h. The solvent was evaporated on a rotary evaporator, and the resulting crude product was dissolved in CH_2Cl_2 (40 mL) and washed with saturated aqueous NH_4Cl (20 mL) and H_2O (20 mL). Drying the CH_2Cl_2 extract over $MgSO_4$ followed by solvent removal under vacuum gave the crude product. Precipitation from CH_2Cl_2/MeOH afforded the pure product (400 mg, 89% yield).

1a. ^{1}H NMR δ, ppm: 0.98 (18H, s, *t*-Bu), 1.36 (18H, S, *t*-Bu), 3.64 (4H, d, $^2J_{HH}$ = 13.5 Hz, CH_2), 4.96 (4H, d, $^2J_{HH}$ = 13.5 Hz, CH_2), 6.04 (2H, s, OH), 6.84−6.87 (4H, m, Ar−H), 6.93 (4H, s, Ar−H), 6.99−7.02 (2H, m, Ar−H), 7.18 (4H, s, Ar−H), 7.51−7.55 (4H, m, Ar−H). ^{13}C NMR δ, ppm: 30.93, 32.00 (CMe_3), 34.13, 34.44 (CMe_3), 37.29 (CH_2), 87.95, 98.14 (C≡C), all aromatic (s): 119.48, 123.85, 124.68, 125.91, 128.19, 128.34, 129.00, 132.06, 142.15, 142.34, 150.94, 152.00.

1b. The compound was obtained in 75% yield after purification by column chromatography. ^{1}H NMR δ, ppm: 0.99 (18H, s, *t*-Bu), 1.38 (18H, S, *t*-Bu), 3.11 (6H, s, CH_3), 3.67 (4H, d, $^2J_{HH}$ = 13.6 Hz, CH_2), 5.03 (4H, d, $^2J_{HH}$ = 13.6 Hz, CH_2), 6.24 (2H, s, OH), 6.48 (4H, m, Ar−H), 6.95 (4H, s, Ar−H), 7.23 (4H, s, Ar−H), 7.34 (4H, m, Ar−H). ^{13}C NMR δ, ppm: 30.95, 32.03 (CMe_3), 34.13, 34.42 (CMe_3), 37.28 (*C*H_2), 54.75 (OCH_3), 86.73, 98.26 (C≡C), all aromatic (s): 114.37, 119.78, 124.65, 125.86, 128.31, 129.09, 133.63, 134.43, 141.98, 142.31, 150.65, 160.02. HR-MS: M+Na measd (calcd) 899.5072 (899.5010), $C_{62}H_{68}O_4$.

1c. The compound was obtained in 65% yield after purification by column chromatography. ^{1}H NMR δ, ppm: 0.99 (18H, s, *t*-Bu), 1.37 (18H, s, *t*-Bu), 2.08 (6H, s, CH_3), 3.64 (4H, d, $^2J_{HH}$ = 13.5 Hz, CH_2), 5.00 (4H, d, $^2J_{HH}$ = 13.5 Hz, CH_2), 6.14 (2H, s, OH), 6.70 (4H, m, Ar−H), 6.94 (4H, s, Ar−H), 7.18 (4H, s, Ar−H), 7.50 (4H, m, Ar−H). ^{13}C NMR δ, ppm: 21.49 (CMe_3), 30.93, 32.02 (CMe_3), 34.12, 34.42 (CMe_3), 37.26 (*C*H_2), 87.40, 98.37 (C≡C), all aromatic (s): 119.40, 124.65, 125.86, 129.03, 129.50, 132.10, 132.79, 137.91, 139.47, 142.05, 150.78, 152.03. HR-MS: M+Na: measd (calcd) 867.5049 (867.5112), $C_{62}H_{68}O_2$.

1d. The compound was obtained in 70% yield after purification by column chromatography. ^{1}H NMR δ, ppm: 0.98 (18H, s, *t*-Bu), 1.35 (18H, s, *t*-Bu), 3.66 (4H, d, $^2J_{HH}$ = 13.6 Hz, CH_2), 4.87 (4H, d, $^2J_{HH}$ = 13.6 Hz, CH_2), 5.81 (2H, s, OH), 6.94 (4H, s, Ar−H), 7.08 (4H, m, Ar−H), 7.19 (4H, s, Ar−H), 7.28 (4H, m, Ar−H). ^{13}C NMR δ, ppm: 30.80, 30.85, 31.93 (CMe_3), 34.15, 34.49 (CMe_3), 37.23 (*C*H_2), 90.32, 96.51 (C≡C), all aromatic (s): 118.68, 124.86, 125.53, 126.04, 127.19, 127.82, 128.31, 132.06, 142.34, 142.85, 151.76. ^{19}F NMR δ, ppm: −63.33 (6F, s, CF_3); HR-MS: M+Na: measd (calcd) 975.4479 (975.4546), $C_{62}H_{62}O_2F_6$. Anal. for $C_{62}H_{62}F_6O_2$: found (calcd) C 77.65 (78.13); H 6.67 (6.56).

1e. The compound was obtained in 75% yield after purification by column chromatography. ^{1}H NMR δ, ppm: 0.95 (18H, s, *t*-Bu), 1.37 (18H, s, *t*-Bu), 3.60 (4H, d, $^2J_{HH}$ = 13.7 Hz, CH_2), 4.74 (4H, d, $^2J_{HH}$ = 13.7 Hz, CH_2), 5.56 (2H, s, OH), 6.91 (4H, s, Ar−H), 7.16 (4H, s, Ar−H), 7.56 (2H, m, Ar−H), 7.81 (4H, m, Ar−H). ^{13}C NMR δ, ppm: 30.22, 30.77, 31.92 (CMe_3), 34.16, 34.51 (CMe_3), 37.09 (*C*H_2), 91.35, 94.81 (C≡C), all aromatic (s): 118.04, 121.83, 124.94, 126.12, 128.94, 131.05, 131.90, 132.57, 142.56, 143.13, 151.45, 152.24. ^{19}F NMR δ, ppm: −63.74 (12F, s, CF_3).

Preparation of 5. Ligand **5** was prepared following the general procedure but using the mixture of two acetylenes: 1.2 equiv of 4-ethynylanisole and 0.9 equiv of 4-ethynyltrifluorotoluene. After purification by silica column chromatography (hexane/CH_2Cl_2 as eluent), the pure product was obtained in 20% yield.

5. ^{1}H NMR δ, ppm: 0.98 (9H, s, *t*-Bu), 0.99 (9H, s, *t*-Bu), 1.36 (18H, s, *t*-Bu), 3.36 (3H, s, OCH_3), 3.67 (4H, d, $^2J_{HH}$ = 13.6 Hz, CH_2), 4.91 (2H, d, $^2J_{HH}$ = 13.6 Hz, CH_2), 4.97 (2H, d, $^2J_{HH}$ = 13.6 Hz, CH_2), 6.01 (2H, s, OH), 6.51 (2H, ABm, Ar−H), 6.94 (2H, s, Ar−H), 6.95 (2H, s, Ar−H), 7.19 (4H, s, Ar−H), 7.37 (2H, ABm, Ar−H), 7.43 (2H, ABm, Ar−H). ^{13}C NMR δ, ppm: 30.21 (CF_3), 30.88, 30.92, 31.98 (CMe_3), 34.14, 34.40, 34.43 (CMe_3), 37.26 (CH_2), 54.76 (OMe), 86.55, 98.52 (C≡C, Ar−OMe), 90.63, 96.27 (C≡C, Ar−CF_3), all aromatic (s): 114.40, 115.60, 118.87, 119.61, 124.72, 124.80, 125.87, 126.01, 128.89, 129.07, 132.26, 133.47, 141.81, 142.40, 142.58, 150.78, 151.55, 151.93, 160.41, 160.66. HR-MS: measd (calcd) 914.4888 (914.4880), $C_{62}H_{65}O_3F_3$.

General Procedure for the Preparation of Complexes 2−4 and 6. To a solution of the free ligand (**1** or **5**) in 2 mL of dry toluene was added a solution of $ZnMe_2$ (2.0 M in toluene, 2.5 equiv, 30 μL, 0.061 mmol). The resulting mixture was stirred at room temperature for 8 h, and the volatiles were evaporated, giving the pure product as an air-sensitive white solid in 100% yield.

2a. ^{1}H NMR δ, ppm: −2.22 (3H, s, $ZnCH_3$), −0.30 (3H, s, $ZnCH_3$), 1.08 (18H, s, *t*-Bu), 1.37 (18H, s, *t*-Bu), 3.79 (4H, d, $^2J_{HH}$ = 14.0 Hz, CH_2), 5.29 (4H, d, $^2J_{HH}$ = 14.0 Hz, CH_2), 6.91−6.92 (6H, m, Ar−H), 7.22 (4H, s, Ar−H), 7.34 (8H, s, Ar−H). ^{13}C NMR δ, ppm: −14.00 (Zn*C*H_3), −7.57 ($ZnCH_3$), 31.16, 31.99 (CMe_3), 34.27, 34.92 (CMe_3), 40.12 (*C*H_2), 90.10, 106.05 (C≡C), all aromatic (s): 123.98, 125.95, 126.08, 127.50, 128.52, 128.84, 131.24, 132.41, 141.38, 141.93, 152.13, 158.65. HR-MS M−Me: measd (calcd) 957.3531 (957.3562), $C_{62}H_{68}O_2Zn_2$.

2b. ^{1}H NMR δ, ppm: −2.20 (3H, s, $ZnCH_3$), −0.20 (3H, s, $ZnCH_3$), 1.10 (18H, s, *t*-Bu), 1.37 (18H, s, *t*-Bu), 3.11 (6H, s, OCH_3), 3.82 (4H, d, $^2J_{HH}$ = 14.0 Hz, CH_2), 5.33 (4H, d, $^2J_{HH}$ = 14.0 Hz, CH_2), 6.55 (4H, m, Ar−H), 7.24 (4H, s, Ar−H), 7.33 (4H, m, Ar−H), 7.35 (4H, s, Ar−H). ^{13}C NMR δ, ppm: −14.16 (Zn*C*H_3), −7.71 ($ZnCH_3$), 31.30, 31.94 (CMe_3), 34.27, 34.89 (CMe_3), 40.34 (*C*H_2), 54.59 (OCH_3) 89.10, 106.59 (C≡C), all aromatic (s):116.18, 125.50, 128.78, 131.35, 133.41, 133.74, 134.72, 140.90, 141.83, 151.63, 158.75, 160.50. FAB-MS: measured (calcd) 1036 (1036). Anal. for $C_{64}H_{72}O_4Zn_2$: found (calcd) C 74.11 (74.19); H 7.04 (7.00).

2c. ^{1}H NMR δ, ppm: −2.21 (3H, s, $ZnCH_3$), −0.24 (3H, s, $ZnCH_3$), 1.08 (18H, s, *t*-Bu), 1.37 (18H, s, *t*-Bu), 1.92 (6H, s, CH_3), 3.81 (4H, d, $^2J_{HH}$ = 14.0 Hz, CH_2), 5.32 (4H, d, $^2J_{HH}$ = 14.0 Hz, CH_2), 6.76 (4H, m, Ar−H), 7.23 (4H, s, Ar−H), 7.32 (4H, m, Ar−H), 7.34 (4H, s, Ar−H). ^{13}C NMR δ, ppm: −14.10 (Zn*C*H_3), −7.60 ($ZnCH_3$), 21.42 (CMe_3), 31.19, 32.01 (CMe_3), 34.27, 34.90 (CMe_3), 40.15 (*C*H_2), 89.57, 106.43 (C≡C), all aromatic (s): 119.43, 125.93, 127.48, 129.38, 131.30, 132.43, 139.03, 139.45, 141.19, 141.85, 151.90, 158.71. FAB-MS: M−Me measd (calcd) 988 (988). Anal. for $C_{64}H_{72}O_2Zn_2$: found (calcd) C 76.62 (76.56); H 7.27 (7.23).

2d. ^{1}H NMR δ, ppm: −2.21 (3H, s, $ZnCH_3$), −0.39 (3H, s, $ZnCH_3$), 1.07 (18H, s, *t*-Bu), 1.36 (18H, s, *t*-Bu), 3.82 (4H, d, $^2J_{HH}$ = 14.1 Hz, CH_2), 5.19 (4H, d, $^2J_{HH}$ = 14.1 Hz, CH_2), 7.17 (8H, s, Ar−H), 7.23 (4H, s, Ar−H), 7.36 (4H, s, Ar−H). ^{13}C NMR δ, ppm: −13.61 (Zn*C*H_3), −7.03 ($ZnCH_3$), 30.80 (CF_3), 31.09, 31.95 (CMe_3), 34.30, 35.03 (CMe_3), 40.07 (CH_2), 92.17, 104.16 (C≡C), all aromatic (s): 125.26, 125.50, 125.53, 126.12, 127.37, 127.65, 130.60, 132.42, 141.89, 142.38, 153.06, 158.38. ^{19}F NMR δ, ppm: −63.12 (6F, s, CF_3). FAB-MS: M−Me measd (calcd) 1112 (1112). Anal. for $C_{64}H_{66}F_6O_2Zn_2$: found (calcd) C 68.97 (69.13); H 6.06 (5.98).

2e. ^{1}H NMR δ, ppm: −2.26 (3H, s, $ZnCH_3$), −0.48 (3H, s, $ZnCH_3$), 1.04 (18H, s, *t*-Bu), 1.36 (18H, s, *t*-Bu), 3.77 (4H, d, $^2J_{HH}$ = 14.0 Hz, CH_2), 5.06 (4H, d, $^2J_{HH}$ = 14.0 Hz, CH_2), 7.22 (4H, s, Ar−H), 7.33 (4H, m, Ar−H), 7.47 (2H, s, Ar−H), 7.79 (4H, s, Ar−H). ^{13}C NMR δ, ppm: −13.81 (Zn*C*H_3), −6.94 ($ZnCH_3$), 30.71 (CF_3), 31.00 (CMe_3), 31.58 (CF_3), 31.91 (CMe_3), 34.30, 35.03 (CMe_3), 39.90 (CH_2), 93.01, 101.96 (C≡C), all aromatic (s): 121.85, 122.23, 124.36, 126.17, 130.79, 131.70, 132.13, 132.47, 142.21, 142.65, 153.73, 158.19. ^{19}F NMR δ, ppm: −62.51 (12F, s, CF_3). FAB-MS: M−Me measd (calcd) 1231 (1231); $C_{66}H_{64}F_{12}O_2Zn_2$.

6. ^{1}H NMR δ, ppm: −2.21 (3H, s, $ZnCH_3$), −0.30 (3H, s, $ZnCH_3$), 1.08 (9H, s, *t*-Bu), 1.09 (9H, s, *t*-Bu), 1.37 (18H, s, *t*-Bu), 3.07 (3H, s, OCH_3), 3.80 (2H, d, $^2J_{HH}$ = 14.1 Hz, CH_2), 3.83 (2H, d, $^2J_{HH}$ = 13.9 Hz, CH_2), 5.25 (2H, d, $^2J_{HH}$ = 13.9 Hz, CH_2), 5.27 (2H, d, $^2J_{HH}$ = 14.1 Hz, CH_2), 6.53 (2H, m, Ar−H), 7.23 (4H, s, Ar−H), 7.28−7.35 (10H, m, Ar−H). ^{13}C NMR δ, ppm: −13.93 (Zn*C*H_3), −7.44 ($ZnCH_3$), 30.21 (CF_3), 31.12, 31.18, 31.98 (CMe_3), 34.28, 34.91, 34.98 (CMe_3), 40.08, 40.19 (CH_2), 54.65 (OMe), 88.94, 107.32 (C≡C, Ar−OMe), 92.42, 103.58 (C≡C, Ar−CF_3), all aromatic (s): 125.93, 126.12, 126.28, 127.52, 127.58, 128.68, 129.09, 131.14, 131.21 132.38, 134.16, 134.43, 140.79, 141.98, 142.08, 151.95, 152.74, 158.59, 160.66, 160.80. Anal. for $C_{64}H_{69}F_3O_3Zn_2$: found (calcd) C 71.22 (71.57); H 6.75 (6.48).

3a (using $ZnEt_2$ 1.0 M in hexane). ^{1}H NMR δ, ppm: −1.37 (2H, q, $^2J_{HH}$ = 7.9 Hz, $ZnCH_2CH_3$), 0.01 (3H, t, $^3J_{HH}$ = 7.9 Hz, $ZnCH_2CH_3$), 0.51 (2H, q, $^2J_{HH}$ = 8.0 Hz, $ZnCH_2CH_3$), 1.14 (18H, s, *t*-Bu), 1.24 (3H, t, $^3J_{HH}$ = 8.0 Hz, $ZnCH_2CH_3$), 1.36 (18H, s, *t*-Bu), 3.80 (4H, d, $^2J_{HH}$ = 13.9 Hz, CH_2), 5.30 (4H, d, $^2J_{HH}$ = 13.9 Hz, CH_2), 6.92−6.94 (6H, m, Ar−H), 7.31 (4H, s, Ar−H),

7.32 (4H, s, Ar−H), 7.40−7.42 (4H, m, Ar−H). ^{13}C NMR δ, ppm: −2.60 (Zn*C*H_2CH$_3$), 5.56 (Zn*C*H_2CH$_3$), 11.22 (ZnCH$_2$*C*H$_3$), 12.78 (ZnCH$_2$*C*H$_3$), 31.05, 32.02 (*C*Me$_3$), 34.24, 35.07 (*C*Me$_3$), 40.19 (*C*H$_2$), 89.60, 105.54 (C≡C), all aromatic (s): 123.98, 125.89, 126.25, 127.58, 128.53, 128.88, 130.74, 132.21, 141.07, 142.00, 152.57, 159.20. FAB-MS: M−Et measd (calcd) 974 (974). Anal. for $C_{64}H_{72}O_2Zn_2$: found (calcd) C 76.20 (76.56); H 7.22 (7.23).

3b. ^{1}H NMR δ, ppm: −1.34 (2H, q, $^2J_{HH}$ = 7.9 Hz, ZnCH$_2$-CH$_3$), 0.03 (3H, t, $^3J_{HH}$ = 7.9 Hz, ZnCH$_2$CH$_3$), 0.62 (2H, q, $^2J_{HH}$ = 7.9 Hz, ZnCH$_2$CH$_3$), 1.16 (18H, s, *t*-Bu), 1.33 (3H, t, overlapped with *t*-Bu at 1.36), 1.36 (18H, s, *t*-Bu), 3.13 (6H, s, OCMe$_3$), 3.84 (4H, d, $^2J_{HH}$ = 13.8 Hz, CH$_2$), 5.35 (4H, d, $^2J_{HH}$ = 13.8 Hz, CH$_2$), 6.56 (4H, m, Ar−H), 7.33 (8H, s, Ar−H), 7.40 (4H, m, Ar−H). ^{13}C NMR δ, ppm: −2.75 (Zn*C*H$_2$CH$_3$), 5.12 (Zn*C*H$_2$CH$_3$), 11.27 (ZnCH$_2$*C*H$_3$), 12.94 (ZnCH$_2$*C*H$_3$), 31.09, 32.03 (*C*Me$_3$), 34.23, 35.04 (*C*Me$_3$), 40.27 (CH$_2$), 54.66 (OCMe$_3$), 88.59, 106.06 (C≡C), all aromatic (s): 114.39, 125.86, 127.54, 128.68, 130.86, 133.88, 134.43, 140.58, 141.91, 151.07, 159.29, 160.51.

3c. ^{1}H NMR δ, ppm: −1.35 (2H, q, $^2J_{HH}$ = 7.9 Hz, ZnCH$_2$-CH$_3$), 0.02 (3H, t, $^3J_{HH}$ = 7.9 Hz, ZnCH$_2$CH$_3$), 0.58 (2H, q, $^2J_{HH}$ = 8.0 Hz, ZnCH$_2$CH$_3$), 1.15 (18H, s, *t*-Bu), 1.30 (3H, t, $^3J_{HH}$ = 8.0 Hz, ZnCH$_2$CH$_3$), 1.36 (18H, s, *t*-Bu), 1.93 (6H, s, CMe$_3$), 3.82 (4H, d, $^2J_{HH}$ = 13.9 Hz, CH$_2$), 5.34 (4H, d, $^2J_{HH}$ = 13.8 Hz, CH$_2$), 6.77 (4H, m, Ar−H), 7.31 (4H, s, Ar−H), 7.33 (4H, s, Ar−H), 7.39 (4H, m, Ar−H). ^{13}C NMR δ, ppm: −2.68 (Zn*C*H$_2$CH$_3$), 5.36 (Zn*C*H$_2$CH$_3$), 11.25 (ZnCH$_2$*C*H$_3$), 12.88 (ZnCH$_2$*C*H$_3$), 21.44 (*C*Me$_3$), 31.07, 32.03 (*C*Me$_3$), 34.24, 35.06 (*C*Me$_3$), 40.23 (CH$_2$), 89.09, 105.91 (C≡C), all aromatic (s): 119.44, 125.87, 127.56, 129.39, 130.81, 132.24, 139.05, 139.45, 140.88, 141.93, 151.32, 159.26.

3d. ^{1}H NMR δ, ppm: −1.36 (2H, q, $^2J_{HH}$ = 7.9 Hz, ZnCH$_2$-CH$_3$), 0.00 (3H, t, $^3J_{HH}$ = 7.9 Hz, ZnCH$_2$CH$_3$), 0.39 (2H, q, $^2J_{HH}$ = 8.0 Hz, ZnCH$_2$CH$_3$), 1.09 (3H, m, overlapped with *t*-Bu at 1.13), 1.13 (18H, s, *t*-Bu), 1.36 (18H, s, *t*-Bu), 3.82 (4H, d, $^2J_{HH}$ = 13.8 Hz, CH$_2$), 5.21 (4H, d, $^2J_{HH}$ = 13.8 Hz, CH$_2$), 7.20−7.27 (8H, m, Ar−H), 7.32 (4H, s, Ar−H), 7.34 (4H, s, Ar−H). ^{13}C NMR δ, ppm: −2.17 (Zn*C*H$_2$CH$_3$), 6.18 (Zn*C*H$_2$CH$_3$), 11.12 (ZnCH$_2$*C*H$_3$), 12.54 (ZnCH$_2$*C*H$_3$), 30.23, 30.719 (*C*F$_3$), 30.96, 31.96 (*C*Me$_3$), 34.26, 35.15 (*C*Me$_3$), 40.14 (CH$_2$), 91.66, 103.67 (C≡C), all aromatic (s): 121.77, 125.46, 126.04, 129.33, 130.11, 130.49, 130.75, 132.22, 141.57, 142.43, 152.50, 158.94. ^{19}F NMR δ, ppm: −63.07 (6F, s, CF$_3$). FAB-MS: M−Et measd (calcd) 1111(1111); $C_{66}H_{70}F_6O_2Zn_2$.

3e. ^{1}H NMR δ, ppm: −1.42 (2H, q, $^2J_{HH}$ = 8.0 Hz, ZnCH$_2$-CH$_3$), −0.06 (3H, t, $^3J_{HH}$ = 8.0 Hz, ZnCH$_2$CH$_3$), 0.27 (2H, q, $^2J_{HH}$ = 8.1 Hz, ZnCH$_2$CH$_3$), 1.09 (3H, t, overlapped with *t*-Bu), 1.11 (18H, s, *t*-Bu), 1.36 (18H, s, *t*-Bu), 3.77 (4H, d, $^2J_{HH}$ = 13.9 Hz, CH$_2$), 5.07 (4H, d, $^2J_{HH}$ = 13.8 Hz, CH$_2$), 7.29 (4H, s, Ar−H), 7.30 (4H, s, Ar−H), 7.49 (2H, s, Ar−H), 7.86 (4H, s, Ar−H). ^{13}C NMR δ, ppm: −2.31 (Zn*C*H$_2$CH$_3$), 5.89 (Zn*C*H$_2$CH$_3$), 11.01 (ZnCH$_2$*C*H$_3$), 12.07 (ZnCH$_2$*C*H$_3$), 30.22 (CF$_3$), 30.59 (CF$_3$), 30.89, 31.95 (CMe$_3$), 34.29, 35.19 (CMe$_3$), 39.98 (CH$_2$), 92.54, 101.51 (C≡C), all aromatic (s): 121.88, 122.21, 124.96, 126.12, 130.29, 131.79, 132.14, 132.48, 141.92, 142.68, 153.19, 158.71. ^{19}F NMR δ, ppm: −62.53 (12F, s, CF$_3$).

4a. ^{1}H NMR δ, ppm: 0.70 (18H, s, *t*-Bu), 1.43 (18H, s, *t*-Bu), 3.77 (4H, d, $^2J_{HH}$ = 14.2 Hz, CH$_2$), 5.27 (4H, d, $^2J_{HH}$ = 14.2 Hz, CH$_2$), 6.74−6.80 (6H, m, Ar−H), 6.92−6.94 (4H, m, Ar−H), 7.07 (4H, s, Ar−H), 7.39 (4H, s, Ar−H). ^{13}C NMR δ, ppm: 30.23, 31.86 (CMe$_3$), 34.42, 34.62 (CMe$_3$), 40.11 (*C*H$_2$), 89.12, 107.84 (C≡C), all aromatic (s): 122.24, 125.58, 125.69, 126.43, 129.25, 129.34, 130.72, 131.78, 141.24, 143.82, 152.78, 157.25. ^{19}F NMR δ, ppm: −113.26 (2F, d, J_{FF} = 19.17 Hz), −115.67 (2F, d, J_{FF} = 20.64 Hz), −157.31 (1F, t, J_{FF} = 18.6 Hz) −158.85 (1F, t, J_{FF} = 18.6 Hz), −161.08 (2F, m), −163.28 (2F, m). HR-MS: M+H measd (calcd) 1277.3213 (1277.3246); $C_{72}H_{63}O_2F_{10}Zn_2$.

4b. ^{1}H NMR δ, ppm: 0.72 (18H, s, *t*-Bu), 1.43 (18H, s, *t*-Bu), 3.18 (6H, s, OCH$_3$), 3.81 (4H, d, $^2J_{HH}$ = 14.2 Hz, CH$_2$), 5.30 (4H, d, $^2J_{HH}$ = 14.2 Hz, CH$_2$), 6.42 (4H, m, Ar−H), 6.93 (4H, m, Ar−H), 7.32 (4H, s, Ar−H), 7.40 (4H, s, Ar−H). ^{13}C NMR δ, ppm: 30.30, 31.89 (CMe$_3$), 34.43, 34.59 (CMe$_3$), 40.22 (*C*H$_2$), 54.89 (OCH$_3$), 88.32, 108.67 (C≡C), all aromatic (s): 113.96, 125.55, 127.01, 129.34, 130.83, 133.66, 140.68, 143.69, 152.24, 157.36, 161.02. ^{19}F NMR δ, ppm: −114.23 (2F, d, J_{FF} = 16.6 Hz), −116.23 (2F, d, J_{FF} = 19.0 Hz), −158.45 (1F, t, J_{FF} = 19.5 Hz) −160.00 (1F, t, J_{FF} = 19.0 Hz), −162.46 (2F, m), −164.35 (2F, m). FAB-MS: measd (calcd) 1340 (1340); $C_{74}H_{66}F_{10}O_4Zn_2$.

4c. ^{1}H NMR δ, ppm: 0.71 (18H, s, *t*-Bu), 1.43 (18H, s, *t*-Bu), 1.95 (6H, s, CH$_3$), 3.79 (4H, d, $^2J_{HH}$ = 14.2 Hz, CH$_2$), 5.30 (4H, d, $^2J_{HH}$ = 14.2 Hz, CH$_2$), 6.66 (4H, m, Ar−H), 6.92 (4H, m, Ar−H), 7.08 (4H, s, Ar−H), 7.39 (4H, s, Ar−H). ^{13}C NMR δ, ppm: 30.27, 31.89 (CMe$_3$), 34.43, 34.61 (CMe$_3$), 40.18 (*C*H$_2$), 88.72, 108.30 (C≡C), all aromatic (s): 119.44, 125.56, 126.71, 128.86, 130.78, 131.89, 139.44, 139.98, 141.05, 143.74, 152.54, 160.62. ^{19}F NMR δ, ppm: −113.24 (2F, d, J_{FF} = 18.3 Hz), −115.45 (2F, d, J_{FF} = 21.2 Hz), −157.40 (1F, t) −160.08 (1F, t), −161.55 (2F, t), −163.34 (2F, t).

4d. ^{1}H NMR δ, ppm: 0.69 (18H, s, *t*-Bu), 1.43 (18H, s, *t*-Bu), 3.79 (4H, d, $^2J_{HH}$ = 14.2 Hz, CH$_2$), 5.17 (4H, d, $^2J_{HH}$ = 14.2 Hz, CH$_2$), 6.75 (4H, m, Ar−H), 7.03 (4H, m, Ar−H), 7.08 (4H, s, Ar−H), 7.40 (4H, s, Ar−H). ^{13}C NMR δ, ppm: 30.17 (CMe$_3$), 30.22 (CF$_3$), 31.83 (CMe$_3$), 34.46, 34.73 (CMe$_3$), 40.72 (*C*H$_2$), 90.85, 105.65 (C≡C), all aromatic (s): 124.29, 126.52, 127.17, 128.92, 129.18, 130.48, 131.45, 132.62, 141.80, 144.27, 153.73, 157.01. ^{19}F NMR δ, ppm: −62.68 (6F, s, CF$_3$), −113.46 (2F, d, J_{FF} = 20 Hz), −115.36 (2F, d, J_{FF} = 20 Hz), −156.89 (2F, m) −160.09 (2F, m), −162.91 (2F, m). FAB-MS: measd (calcd) 1392 (1392); $C_{72}H_{60}F_{16}O_2Zn_2$.

Computational Methods. All calculations were carried out using Gaussian 03 Revision C.02.[19] Geometry optimizations were carried out using the PBE0 DFT exchange−correlation functional together with the SDD basis set. PBE0 is the hybride variant of PBE (Perdew, Burke, and Ernzerhof's nonempirical GGA functional) and contains 25% HF exchange.[20] This functional has been shown to yield more reliable reaction barrier heights than B3LYP[23] or other "conventional" exchange−correlation functionals, without sacrificing performance of other properties.[24] SDD is the combination of the Huzinaga−Dunning double-ζ basis set[21] on lighter elements with the Stuttgart−Dresden basis set−RECP combination[22] on transition metals. Geometries were optimized using the default pruned (75 302) grid.

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Supporting Information Available: Crystallographic information for complexes **2a** and **6** (CIF). Complete ref 19. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) (a) Stevens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(24) Quintal, M. M.; Karton, A.; Iron, M. A.; Boese, A. D.; Martin, J. M. L. *J. Phys. Chem. A* **2006**, *110*, 709.