reflections. Crystal data and intensity collections parameters are given in Table IV. The intensities of three reflections (006, $\bar{5}22$, $\bar{4}20$) were monitored every hour of exposure and showed no evidence of decay. For all subsequent computations the Enraf-Nonius SDP package was used.[24] Data were corrected for Lorentz polarization and for absorption using the DIFABS program[25] (absorption coefficients minimum 0.951, maximum 1.024). The crystal structure was solved by using the Patterson and Fourier difference methods and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. The function minimized was $\sum(w|F_o| - |F_c|)^2$, where the weight w is $[4F_o^2]/[\sigma^2(F_o) - (0.07|F_o|^2)]$. Hydrogen atoms were placed in calculated positions (C–H distances 0.95 Å) in structure factor calculations and were assigned isotropic thermal parameters of $B = 5$ Å^2, except for the hydrido H, which was positioned by Fourier difference and refined isotropically. A final difference map revealed no significant residual peak. Neutral atom scattering factors used for all atoms and anomalous dispersion coefficients were obtained from standard sources.[26] The positional parameters obtained from the last cycle of refinement are listed in Table V, with the corresponding standard deviations.

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Supplementary Material Available: Projection of the structure of **2b** perpendicular to the Co_3 plane (Figure S-1), complete set of bond angles (Table S-I), and temperature factors for anisotropic atoms (Table S-II) (4 pages). Ordering information is given on any current masthead page.

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Control of Donor–Acceptor Interactions in Organoalkaline-Earth–Transition-Metal Complexes. Crystallographic Characterization of $(Me_5C_5)_2HfCl(\mu\text{-}Cl)Ca(Me_5C_5)_2$

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The problem of ligand exchange or loss in the formation of organometallic alkaline-earth–transition-metal complexes can be minimized by ensuring that any exchange would be degenerate or would require an unfavorable transfer of ligands. This approach is illustrated in the formation of chloride-bridged calcium–group 4 dimers and in an isocarbonyl-linked calcium–chromium dimer. Bis(pentamethylcyclopentadienyl)calcium Cp^*_2Ca, reacts with $Cp^*_2ZrCl_2$, $Cp^*_2HfCl_2$, and $Cp^*_2ThCl_2$ in toluene to yield 1:1 adducts. Orange-yellow crystals of $Cp^*_2HfCl(\mu\text{-}Cl)CaCp^*_2$ grown from toluene are triclinic, space group $P\bar{1}$, with $a = 11.146$ (4) Å, $b = 16.942$ (6) Å, $c = 11.109$ (3) Å, $\alpha = 103.34$ (3)°, $\beta = 94.89$ (3)°, $\gamma = 102.50$ (3)°, and D(calcd) = 1.398 g cm^{-3} for $Z = 2$. The structure consists of two bent metallocene units with a single μ-Cl and a terminal Cl on hafnium: Ca–μ-Cl = 2.864 (3) Å, Hf–μ-Cl = 2.463 (3) Å, Hf–Cl(t) = 2.383 (3) Å, and Ca–Cl–Hf = 161.3 (1)°. Cp^*_2Ca reacts with $Cp^*_2Zr(CO)_2$ and mesitylenechromium tricarbonyl in toluene in yield 1:1 adducts. In the solid state, the calcium–chromium adduct exists as a tetranuclear species, constructed around a 12-membered ring consisting of two Ca and Cr atoms and four carbonyl groups.

The heavy alkaline-earth (Ae) elements calcium, strontium, and barium are being increasingly incorporated into a range of solid-state materials with diverse electronic and chemical properties, including the high-temperature superconductors (e.g., $YBa_2Cu_3O_{7-x}$),[1-3] "hydrogen storage" alloys (e.g., $CaNi_5$),[4] and perovskite-based methane oxidation catalysts (e.g., ABO_3 (A = Ca, Sr, Ba; B = Ti, Zr, Ce)).[5,6] Rational syntheses of discrete polymetallic group 2–transition-metal complexes that might serve either as precursors to or as models of these nonmolecular solids have been limited to O-bound (primarily alkoxide) species,[7] and facile ligand exchange or loss can make controlling the composition of these systems difficult.[8]

Table I. ^1H NMR Shifts of Heterometallic Compounds

compd	heterometallic subunits $(C_5Me_5)Ca$	heterometallic subunits $(C_5Me_5)M$	parent $(C_5Me_5)ME_2$	ref
$Cp^*_2Ca(Cl)_2ZrCp^*_2$	2.04	1.80	1.84	17
$Cp^*_2Ca(Cl)_2HfCp^*_2$	1.95	1.89	1.90	15
$Cp^*_2Ca(Cl)_2ThCp^*_2$	2.14	2.09	2.02	18
$Cp^*_2Ca(OC)_2ZrCp^*_2$	2.07	1.70	1.73	16
$Cp^*_2Ca(\mu\text{-}OC)_2(OC)$-Cr(mes)	2.15	(4.13, 1.64)[a]	(4.07, 1.66)[a]	22

[a] The values for the ring and methyl protons, respectively, of the mesitylene group.

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The decamethylmetallocenes of Ca, Sr, and Ba have proven to be useful hydrocarbon-soluble Lewis acids that can bind to Lewis bases, including ethers, aromatic amines, phosphines, isonitriles,[9] and, most recently, alkynes.[10] The facility with which these adducts are formed suggests that their reaction with nucleophilic transition-metal species would offer a systematic route to the formation of *s*-block-*d*-block species, if the problem of unfavorable ligand exchange could be controlled. We now report synthetic strategies that allow such complexes to be successfully prepared, using Cp^*_2Ca ($Cp^* = C_5Me_5$)[9,11] as the alkaline-earth substrate.

Experimental Section

All manipulations were performed with the rigid exclusion of air and moisture. Chemicals were handled with high vacuum or Schlenk techniques or in a Vacuum Atmospheres HE-143 drybox equipped with an MO40-1 recirculating purifier. Proton NMR spectra were obtained at 300 MHz with a Bruker NR-300 spectrometer and were referenced to the residual proton resonances of C_6D_6 (δ 7.15); they are listed in Table I. Carbon (^{13}C) NMR spectra were recorded at 50.3 MHz on a Bruker NR-200 spectrometer and were referenced to the residual ^{13}C resonances of C_6D_6 (δ 128.0). Infrared data were obtained on a Perkin-Elmer 1430 spectrometer as saturated solutions in toluene or a KBr pellet as previously described.[12] Elemental analyses were performed by Oneida Research Services, Whitesboro, NY, but were often marked by low C and H values. This problem has been observed in other organoalkaline-earth systems.[13,14]

Materials. $Cp^*_2HfCl_2$ ($Cp^* = C_5Me_5$),[15] $Cp^*_2HfH_2$,[15] and $Cp^*_2Zr(CO)_2$[16] were prepared according to published procedures. $Cp^*_2ZrCl_2$ was prepared analogously to $Cp^*_2HfCl_2$, substituting $ZrCl_4$ for $HfCl_4$.[17] $Cp^*_2ThCl_2$ was made according to the literature procedure, substituting KCp* for Cp*MgCl.[18] Mesitylenechromium tricarbonyl was prepared by refluxing $Cr(CO)_6$ in mesitylene and recrystallizing from diethyl ether.[19]

$Cp^*_2CaCl(\mu$-$Cl)ZrCp^*_2$ from Cp^*_2Ca and $Cp^*_2ZrCl_2$. Cp^*_2Ca (0.200 g, 0.644 mmol) and $Cp^*_2ZrCl_2$ (0.276 g, 0.638 mmol) were placed in 50 mL of toluene and stirred for 10 h. The resulting clear brown filtrate was evaporated to dryness, leaving 0.416 g (89%) of the title compound as a brown, friable solid. Anal. Calcd for $C_{40}H_{60}CaCl_2Zr$: C, 64.65; H, 8.14; Zr, 12.28. Found: C, 53.14; H, 6.78; Zr, 9.27. Although the C, H values are low, the C:H ratio is 0.66, in agreement with the predicted value. ^{13}C NMR (C_6D_6, 20 °C, saturated solution, proton decoupled): δ 123.9 ((C_5Me$_5$)$_2$Zr); 113.8 ((C_5Me$_5$)$_2$Ca); 12.0 ((C$_5$*Me*$_5$)$_2$Ca); 10.8 ((C$_5$*Me*$_5$)$_2$Zr).

$Cp^*_2CaCl(\mu$-$Cl)HfCp^*_2$ from Cp^*_2Ca and $Cp^*_2HfCl_2$. $Cp^*_2HfCl_2$ (0.200 g, 0.385 mmol) was dissolved in 50 mL of toluene. To this solution, Cp^*_2Ca (0.120 g, 0.386 mmol) was added, and the initial pale yellow solution turned brownish orange within a few seconds. After stirring for 1 h, the clear solution was evaporated to dryness, giving 0.290 g (91% yield) of pale yellow $Cp^*_2Ca(Cl)ClHfCp^*_2$. This solid was redissolved in toluene, concentrated, and cooled to −43 °C. Orange-yellow crystals of the compound were deposited from the cold toluene solution after several days. Anal. Calcd for $C_{40}H_{60}CaCl_2Hf$: C, 57.86; H, 8.54; Hf, 21.49. Found: C, 52.15; H, 6.62; Hf, 20.96. Although the C, H values are low, the C:H ratio is 0.66, in agreement with the expected value. ^{13}C NMR (C_6D_6, 20 °C, saturated solution, proton decoupled): δ 121.9 ((C_5Me$_5$)$_2$Hf), 114.0 ((C_5Me$_5$)$_2$Ca), 11.9 ((C$_5$*Me*)$_2$Ca), 10.6 ((C$_5$*Me*$_5$)$_2$Hf).

$Cp^*_2CaCl(\mu$-$Cl)ThCp^*_2$ from Cp^*_2Ca and $Cp^*_2ThCl_2$. $Cp^*_2ThCl_2$ (0.382 g, 0.666 mmol) was placed in 50 mL of toluene. Cp^*_2Ca (0.207 g, 0.667 mmol) was added to the solution and the mixture stirred for 12 h. The slightly turbid solution was gravity filtered through a medium glass frit. The colorless filtrate was evaporated to dryness, giving 0.44 g (75%) of white $Cp^*_2Ca(Cl)_2ThCp^*_2$. Anal. Calcd for $C_{40}H_{60}CaCl_2Th$: C, 54.35; H, 6.84. Found: C, 47.82; H, 6.06. Although the C, H values are low, the C:H ratio is 0.66, in agreement with the predicted value. ^{13}C NMR (C_6D_6, 20 °C, saturated solution, proton decoupled: δ 112.9 ((C_5Me$_5$)$_2$Ca), 11.5 ((C$_5$*Me*$_5$)$_2$Th), 11.2 ((C$_5$*Me*$_5$)$_2$Ca). The quaternary carbons associated with the thorium were not observed, presumably because of the low solubility of the complex.

$Cp^*_2Ca(\mu$-$OC)_2(OC)Cr(mes)$ from Cp^*_2Ca and $(mes)Cr(CO)_3$ (mes = 1,3,5-$C_6H_3Me_3$). Cp^*_2Ca (0.200 g, 0.644 mmol) and $(mes)Cr(CO)_3$ (0.166 g, 0.648 mmol) were dissolved in 30 mL of toluene and stirred for 12 h. The resulting slightly turbid solution was gravity filtered through a medium glass frit. The brownish orange filtrate was dried by rotary evaporation to give 0.25 g of a brown, friable solid. ^1H NMR spectra from different preparations indicate that the solid retains variable amounts of toluene, although it averages near 1 equiv per $(mes)Cr(CO)_3$. Anal. Calcd for $C_{32}H_{42}CaCrO_3{\cdot}C_7H_8$: C, 71.09; H, 7.65; Cr, 7.89. Found: C, 66.68; H, 6.77; Cr, 8.03. A concentrated toluene solution cooled to −43 °C will deposit orange X-ray quality crystals. ^{13}C NMR (C_6D_6, 20 °C, saturated solution, proton decoupled): δ 112.4 (C_5Me$_5$), 92.2 (C_6H$_3$Me$_3$), 20.3 (C$_6$H$_3$*Me*$_3$), 11.2 (C$_5$*Me*$_5$). Owing to the limited solubility of the compound, the peaks associated with the ring carbons were observed only with difficulty; the carbonyl carbons were not observed in the ^{13}C NMR spectra, despite attempts using long pulse delays. IR (major bands, toluene, cm^{-1}): ν(CO) 1956, 1884, 1830, 1748.

$Cp^*_2Ca(OC)_2ZrCp^*_2$ from Cp^*_2Ca and $Cp^*_2Zr(CO)_2$. $Cp^*_2Zr(CO)_2$ (0.269 g, 0.644 mmol) was dissolved in 25 mL of stirring toluene. To the black solution, Cp^*_2Ca (0.200 g, 0.644 mmol) was added and the solution stirred for 5 h, during which time the solution turned reddish black. Removal of the solvent by rotary evaporation left 0.46 g (98%) of a black, friable solid. Anal. Calcd for $C_{42}H_{60}CaO_2Zr$: C, 69.27; H, 8.30; Zr, 12.53. Found: C. 68.64; H, 8.36; Zr, 12.71. ^{13}C NMR (C_6D_6, 20 °C, saturated solution, proton decoupled): δ 113.5 ((C_5Me$_5$)$_2$Ca); 106.8 ((C_5Me$_5$)$_2$Zr); 10.9 (C$_5$*Me*$_5$)$_2$Zr); 10.8 ((C$_5$*Me*$_5$)$_2$Ca). The carbonyl carbons were not observed. IR (major bands, toluene, cm^{-1}): ν(CO) 1939 (s), 1843 (s), 1776 (s). IR (major bands, KBr, cm^{-1}): ν(CO) 1930 (s), 1828 (s), 1758 (s).

Attempted Reaction of Cp^*_2Ca with $Cp^*_2HfH_2$. $Cp^*_2HfH_2$ (0.100 g, 0.222 mmol) was dissolved in 60 mL of toluene. Cp^*_2Ca (0.069 g, 0.222 mmol) was added to this solution and the reaction mixture stirred for 48 h. Removal of the solvent gave a slightly brown residue, but its ^1H NMR (C_6D_6, 20 °C) spectrum revealed it to be only a mixture of starting materials.

X-ray Crystallography of $Cp^*_2CaCl(\mu$-$Cl)HfCp^*_2$. Crystals of $Cp^*_2CaCl(\mu$-$Cl)HfCp^*_2$ were grown from toluene. A suitable prism measuring 0.56 × 0.40 × 0.35 mm was located and sealed in a quartz capillary tube. All measurements were performed on a Rigaku AFC6S diffractometer with graphite monochromated Mo Kα radiation. Data were collected at 20 ± 1 °C. Relevant crystal and data collection parameters for the present study are given in Table II.

Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $20.6 < 2\theta < 26.0°$. Based on unit cell parameters and a statistical analysis of intensity distribution, the space group was determined to be triclinic $P\bar{1}$, a choice confirmed by subsequent solution and refinement of the structure. Data collection was performed using a continuous ω–2θ scan with stationary backgrounds. The intensities of three representative reflections measured after every

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Table II. Crystal Data and Summary of Data Collection for $Cp^*_2HfCl(\mu\text{-}Cl)CaCp^*_2$

formula	$C_{40}H_{60}CaCl_2Hf$
fw	830.39
color of crystal	orange-yellow
cryst dimens, mm	0.56 × 0.40 × 0.35
space group	$P\bar{1}$
cell dimens (at 20 °C)	
a, Å	11.146 (4)
b, Å	16.942 (6)
c, Å	11.109 (3)
α, deg	103.34 (3)
β, deg	94.89 (3)
γ, deg	102.50 (3)
V, Å^3	1973 (2)
Z	2
D(calcd), g/cm^3	1.398
wavelength, Å	0.71069
abs coeff, cm^{-1}	29.1
type of scan	ω-2θ
scan speed, deg/min	2
scan width, deg	1.10 + 0.30 tan θ
bkgd counting	stationary counts; peak/background counting time = 2:1
limits of data collection	$6 \leq 2\theta \leq 45°$
total no. of reflns collected	5658
no. of unique intensities	5263
no. with $F > 3.0\sigma(F)$	3887
$R(F)$	0.040
$R_w(F)$	0.046
goodness of fit	1.40
max Δ/σ in final cycle	0.01
max/min peak (final diff map, e–/Å^3)	1.50/–0.70

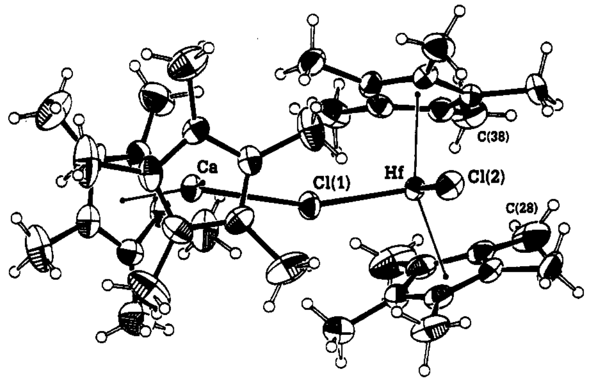

Figure 1. ORTEP view of $Cp^*_2HfCl(\mu\text{-}Cl)CaCp^*_2$, with the nonhydrogen atoms drawn at the 35% probability level.

150 reflections declined by 6%; a linear correction factor was applied to the data to account for the decay. An empirical absorption correction, based on azimuthal scans of several reflections, was applied that resulted in transmission factors ranging from 0.87 to 1.00. Data were reduced to a unique set of intensities and associated σ values in the usual manner. The structure was solved by a combination of direct methods (MITHRIL and DIRDIF) and Fourier techniques. All non-hydrogen atoms were refined anisotropically. As not all the hydrogens were evident on a difference Fourier map, their positions were calculated using idealized geometries based on packing considerations and d(C–H) = 0.95 Å. The positions were fixed for the final cycles of refinement. A final difference map was featureless. Positional parameters are supplied in Table III, average bond distances and angles are listed in Table IV, and an ORTEP drawing is given in Figure 1.

Results and Discussion

A prominent feature of organoalkaline-earth chemistry is the high kinetic lability of its complexes, a consequence of the noble gas configuration of the Ae^{2+} ions.[20] Whether such lability is a synthetic handicap or not depends markedly on the system under investigation. In the formation of donor–acceptor adducts between alkaline-earth decamethylmetallocenes and neutral organic bases, for example, kinetic lability is of little concern, as the electrostatic attraction between the Cp^{*-} and Ae^{2+} ions preserves the integrity of the ligand sets on the metals. In other cases, ligand exchange between alkaline-earth compounds can be constructively useful, as in the formation of monocyclopentadienyl complexes from the conproportionation of metallocenes and dihalides (eq 1).[13]

$$Cp^*_2Ca + CaX_2 \rightarrow 2Cp^*CaX \qquad (1)$$

Table III. Fractional Coordinates and Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms in $Cp^*_2HfCl(\mu\text{-}Cl)CaCp^*_2$

atom	x/a	y/b	z/c	B_{iso}^{a}
Hf(1)	0.50029 (4)	0.27300 (3)	0.63044 (4)	2.80 (1)
Ca(1)	0.8542 (2)	0.2301 (1)	0.9357 (2)	3.44 (7)
Cl(1)	0.6880 (2)	0.2756 (2)	0.7674 (2)	3.98 (9)
Cl(2)	0.3714 (2)	0.2873 (2)	0.7908 (2)	4.3 (1)
C(1)	0.6638 (9)	0.2154 (6)	1.0632 (8)	3.7 (4)
C(2)	0.733 (1)	0.1626 (6)	1.0980 (9)	4.0 (4)
C(3)	0.847 (1)	0.2129 (8)	1.1679 (9)	4.8 (4)
C(4)	0.847 (1)	0.2962 (7)	1.173 (1)	4.7 (4)
C(5)	0.732 (1)	0.2959 (6)	1.107 (1)	4.3 (4)
C(6)	0.529 (1)	0.1860 (9)	0.999 (1)	6.5 (5)
C(7)	0.689 (1)	0.0688 (8)	1.073 (1)	7.5 (6)
C(8)	0.943 (1)	0.183 (1)	1.240 (1)	8.8 (7)
C(9)	0.945 (1)	0.374 (1)	1.241 (1)	8.4 (6)
C(10)	0.689 (1)	0.3736 (8)	1.093 (1)	7.5 (6)
C(11)	1.0681 (9)	0.2970 (6)	0.873 (1)	4.0 (4)
C(12)	1.097 (1)	0.2477 (8)	0.950 (1)	4.6 (4)
C(13)	1.045 (1)	0.1635 (7)	0.886 (1)	5.0 (5)
C(14)	0.9855 (9)	0.1622 (7)	0.767 (1)	4.4 (4)
C(15)	1.0011 (8)	0.2440 (7)	0.760 (1)	3.9 (4)
C(16)	1.112 (1)	0.3901 (8)	0.904 (1)	7.0 (6)
C(17)	1.187 (1)	0.278 (1)	1.070 (1)	8.3 (7)
C(18)	1.061 (1)	0.0878 (9)	0.931 (1)	8.6 (7)
C(19)	0.925 (1)	0.0847 (8)	0.663 (1)	7.7 (6)
C(20)	0.970 (1)	0.2740 (9)	0.644 (1)	6.5 (6)
C(21)	0.643 (1)	0.4151 (6)	0.645 (1)	4.4 (4)
C(22)	0.604 (1)	0.3745 (6)	0.519 (1)	4.5 (4)
C(23)	0.475 (1)	0.3690 (6)	0.494 (1)	4.3 (4)
C(24)	0.437 (1)	0.4024 (6)	0.605 (1)	4.4 (4)
C(25)	0.540 (1)	0.4302 (6)	0.698 (1)	4.2 (4)
C(26)	0.777 (1)	0.4482 (7)	0.706 (1)	7.6 (6)
C(27)	0.690 (1)	0.3547 (8)	0.423 (1)	8.3 (7)
C(28)	0.399 (1)	0.3546 (7)	0.368 (1)	7.8 (6)
C(29)	0.308 (1)	0.4166 (7)	0.619 (1)	6.8 (6)
C(30)	0.544 (1)	0.4779 (7)	0.834 (1)	6.4 (5)
C(31)	0.4963 (9)	0.1182 (6)	0.5932 (9)	3.7 (4)
C(32)	0.5343 (9)	0.1435 (6)	0.4877 (9)	3.6 (4)
C(33)	0.433 (1)	0.1619 (6)	0.4257 (9)	4.1 (4)
C(34)	0.3337 (9)	0.1541 (6)	0.497 (1)	4.1 (4)
C(35)	0.3733 (9)	0.1224 (6)	0.5991 (9)	3.6 (4)
C(36)	0.568 (1)	0.0775 (6)	0.672 (1)	5.1 (4)
C(37)	0.654 (1)	0.1384 (7)	0.439 (1)	5.6 (5)
C(38)	0.425 (1)	0.1661 (7)	0.290 (1)	6.3 (5)
C(39)	0.204 (1)	0.1620 (7)	0.463 (1)	6.2 (5)
C(40)	0.289 (1)	0.0922 (7)	0.686 (1)	5.8 (5)

[a] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609–610.

Table IV. Average Bond Lengths (Å) and Angles (deg) in $Cp^*_2Ca(\mu\text{-}Cl)ClHfCp^*_2$

	parameters	
	Ca–Cp*	Hf–Cp*
M–C(ring) (av)	2.65 (3)	2.52 (3)
C–C(ring) (av)	1.40 (3)	1.40 (3)
C(ring)–C(methyl) (av)	1.52 (3)	1.51 (3)
M–ring centroid (av)	2.37	2.22
centroid–M–centroid	144.2	137.4
av displacement of CH_3 groups from ring plane	4.7	8.0

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Facile ligand exchange can become a serious impediment to the formation of bimetallic complexes between the alkaline earths and transition-metal or *f*-block elements, however. For example, in contrast in eq 1, the reaction of Cp^*_2Ca with YbI_2 does not produce a heterometallic $Cp^*Ca(\mu\text{-}I)_2YbCp^*$ complex but rather a mixture of $Cp^*_2Yb(THF)$[21] and $CaI_2(THF)_2$ (eq 2).[22] Differences in

$$Cp^*_2Ca + YbI_2 \xrightarrow{THF} Cp^*_2Yb(THF) + CaI_2(THF)_2 \quad (2)$$

the relative "hardness" of Ca^{2+} and Yb^{2+} may be a principle driving force here, although in other cases several factors may direct ligand rearrangement. For instance, Cp^*_2Ca reacts with $(dppe)NiCl_2$ in a manner consistent with eq 3,[22] illustrating the effects of hard/soft-acid/base (HSAB)

$$Cp^*_2Ca + (dppe)NiCl_2 \xrightarrow{toluene} Cp^*_2Ni + CaCl_2\downarrow + Ph_2PCH_2CH_2PPh_2 \quad (3)$$

pairing[23] (transfer of Cp^{*-} to Ni^{2+}), relative solubilities (precipitation of $CaCl_2$), and entropic forces (release of the diphosphine).

Controlling Ligand Exchange. One way in which the effects of ligand exchange can be minimized in the formation of heterometallic complexes is by providing identical sets of ligands for both the alkaline-earth and transition-metal species so that any exchange of ligands will be degenerate. This approach, while effective (see below), places substantial restrictions on the ligands that can be used on the transition-metal center.

An alternative method is to ensure that rearrangements occurring because of HSAB preferences will be disfavored. Using "soft" neutral ligands (e.g., CO, PR_3, arenes) on the transition-metal complex will create a situation in which exchange is unfavorable, as these are at best only weakly bound to alkaline-earth ions.[9] The ubiquity of such ligands in transition-metal chemistry provides a far larger selection of potential donors for a mixed-metal complex. The success of these strategies in controlling ligand exchange is illustrated in the formation of chloride-bridged and isocarbonyl-linked calcium-transition-metal dimers.

Formation of Chloride-Bridged Dimers. Upon mixing toluene solutions of Cp^*_2Ca and $Cp^*_2MCl_2$ under nitrogen, brown and brownish orange solutions form when M = Zr and Hf, respectively, but no color change occurs when M = Th. In each case, proton NMR spectra indicate that the methyl resonances assigned to the Cp^*_2Ca unit have shifted downfield by 0.04–0.23 ppm from the value in uncomplexed Cp^*_2Ca (δ 1.91)[9] (Table I). The methyl ring protons on the transition-metal unit display somewhat smaller resonance shifts from the value in the uncomplexed compound ($\Delta\delta$ = 0.01–0.07) but enough to indicate that the environment around their metal centers has been altered. The chemical shifts in these compounds and the carbonyl complexes are slightly concentration dependent, suggesting that an equilibrium may be present between the starting monomers and the adducts. Although crystals suitable for X-ray diffraction could be grown only for the Ca–Hf complex, the NMR shifts in the Zr and Th complexes suggest that they are probably isostructural.

Structure of $Cp^*_2CaCl(\mu\text{-}Cl)HfCp^*_2$. Details of the metal coordination environments in the Ca–Hf compound were revealed in a single-crystal X-ray structure determination. The complex consists of two bent metallocene units with a single μ-Cl and a terminal Cl on hafnium; the centroids of the Cp* rings form a distorted tetrahedron (Figure 1). The average Hf–C(ring) distance of 2.52 (3) Å is similar to that observed in other eight-coordinate (pentamethylcyclopentadienyl)hafnium complexes (e.g., 2.56 (2) Å in $Cp^*_2HfBr_2$[24]; 2.52 (3) Å in $Cp^*_2Hf(H)(NHMe)$[25]). The Ca–Cl–Hf angle is slightly bent at 161.3 (1)°, and the bridging Cl is more closely associated with Hf(Hf–Cl(1) = 2.463 (3) Å) than with Ca (Ca–Cl(1) = 2.864 (3) Å). Predictably, the distance from Hf to the bridging Cl is longer (by 0.08 Å) than to the terminal Cl (Hf–Cl(2) = 2.383 (3) Å). The extent of interaction of the μ-Cl with Ca can be judged by the average Ca–C(ring) distance of 2.65 (3) Å, which is approximately that expected for a seven-coordinate Ca^{2+} ion.[26] For comparison, the analogous distances in $[Cp^*Ca(\mu\text{-}I)(THF)_2]_2$[13] and $\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2Ca(THF)$[27] (both seven-coordinate) are 2.67 (1) and 2.678 (8) Å, respectively.

The structure is remarkably paralleled by the homometallic $Cp^*_2Y(\mu\text{-}Cl)ClYCp^*_2$ dimer reported by Evans, which also contains a single bridging and terminal Cl ligand and is constructed around comparably electropositive elements.[28] The different charges on the metal centers lead to different "effective chloride radii" (M–Cl distance minus M radius) for the bridging Cl in each dimer. In the Ca–Hf dimer, the chloride radius is 1.80 Å relative to Ca^{2+} (seven-coordinate, 1.06 Å[29]) and 1.63 Å relative to Hf^{4+} (eight-coordinate, 0.83 Å). In the yttrium dimer, the chloride radius is 1.68 Å relative to the seven-coordinate Y^{3+} (0.96 Å) and 1.76 Å relative to the eight-coordinate Y^{3+} (1.019 Å). The radii for the terminal chlorides, however, are nearly the same: that of the chloride on Hf^{4+} is 1.55 Å and that for Y^{3+} is 1.56 Å. Both complexes display evidence of overcrowding, which is probably the reason they adopt asymmetric rather than symmetric $Cp^*_2M(\mu\text{-}Cl)_2M'Cp^*_2$ geometries.[28] In the Ca–Hf complex, for example, the Cp* rings on Hf are bent sufficiently far back that substantial distortions in their geometry are apparent: methyl group C(38), for example, lies 16.8° out of the cyclopentadienyl ring plane, and its counterpart on the other ring, C(28), is bent by 15.2°. Even with the bending, these two methyl groups are separated by only 3.19 Å, far less than the sum of the van der Waals' radii (4.0 Å).[30]

$Cp^*_2Ca(OC)_2ZrCp^*_2$ from Cp^*_2Ca and $Cp^*_2Zr(CO)_2$. When Cp^*_2Ca is added to a stirring toluene solution of $Cp^*_2Zr(CO)_2$, there is a slight color change from black to a reddish black. Removal of the solvent leaves a black solid. Its ^1H NMR spectrum reveals shifts in the Cp* resonances for the Ca and Zr units, evidence that some interaction is occurring between the complexes. More definitive data are provided by the solution IR spectrum taken in toluene, which contains three ν(CO) stretches at 1939, 1844, and 1776 cm^{-1}. The first two of these are identical to those observed in uncomplexed $Cp^*_2Zr(CO)_2$ (although in the Ca–Zr mixture the peak at 1939 cm^{-1} is of somewhat greater intensity than that at 1844 cm^{-1}). The third peak is in the region for a bridging CO and is what might be expected for an isocarbonyl ($Ca\cdots O{\equiv}C{-}Zr$) linkage.[31,32] It is not clear exactly what type of connec-

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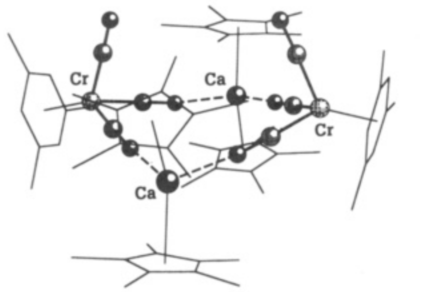

Figure 2. Proposed structure of $[Cp^{*}_{2}Ca(\mu\text{-}OC)_2(OC)Cr(mes)]_2$. Suggested isocarbonyl interactions between the calcium atoms and the carbonyl oxygens (gray spheres) are indicated by dashed lines; the molecules of toluene found in the lattice are omitted.

tivity exists in solution, although there is apparently an equilibrium mixture of uncomplexed and complexed $Cp^{*}_{2}Zr(CO)_2$. Considering the steric demands of the ligands involved, a structure similar to that observed for the chloride-bridged complexes (i.e., $Cp^{*}_{2}Ca(\mu\text{-}OC)(OC)\text{-}ZrCp^{*}_{2}$) may be involved. Attempts to grow crystals suitable for X-ray diffraction study were not successful.

$[Cp^{*}_{2}Ca(\mu\text{-}OC)_2(OC)Cr(mes)]_2$ from $Cp^{*}_{2}Ca$ and $(mes)Cr(CO)_3$. Mixing toluene solutions of $Cp^{*}_{2}Ca$ and $(mes)Cr(CO)_3$ (mes = 1,3,5-$C_6H_3Me_3$) produces a brown solution, which deposits orange crystals on cooling to −43 °C. The proton NMR spectrum of the compound (C_6D_6, 300 MHz, 20 °C) displays the resonances expected for mesitylene at δ 1.64 and 4.13 (shifted from δ 1.66 and 4.07) and that for Cp* at δ 2.15. The ^{13}C NMR resonances of the rings are slightly shifted compared to the parent molecules (cf. δ 112.4 (C_5Me_5) and 11.2 ($C_5\mathit{Me}_5$) in $Cp^{*}_{2}Ca$;[9] 92.2 ($C_6H_3Me_3$) and 20.3 ($C_6H_3\mathit{Me}_3$) in $(mes)Cr(CO)_3$), but the carbonyl carbons were not observed. In toluene solution, the $\nu(CO)$'s of $(mes)Cr(CO)_3$ (1956, 1883 cm^{-1}) are reduced to 1956, 1884, 1830, and 1748 cm^{-1} in the polymetallic species, a change typical of the effect seen in complexes containing isocarbonyl linkages.[31,32]

Only poorly diffracting crystals of the complex could be grown from toluene, but these were sufficient to establish the general geometry by X-ray diffraction.[33] In the solid state, the adduct exists as a tetranuclear species, $[Cp^{*}_{2}Ca(\mu\text{-}OC)_2(OC)Cr(mes)]_2\cdot 2(toluene)$, constructed around a 12-membered ring containing 2 Ca and Cr atoms and 4 carbonyl groups (Figure 2). Two molecules of toluene per dimer are found in the lattice; one of them is disordered, but neither is closer than 3.5 Å from the mesitylenes. Two of the carbonyl groups from each chromium fragment display apparent isocarbonyl (M–CO···M′) interactions with the calcium atoms, with Ca···O distances ranging from 2.44 to 2.55 Å and CO···M′ angles varying from 162 to 177°. The remaining carbonyl group of each chromium unit remains terminal, oriented toward the center of the same side of the ring.

Related [M···O–C–M′–C–C···]$_2$ frameworks have been observed in Mo–Ti,[34] Co–Ti,[35] W–Al,[36] Yb–Mn,[37] Sm–Fe,[38] and Ce–W systems,[39] although, unlike the Ca–Cr complex, all of these can formally be considered to be ion-paired species. The closest structural parallels with the present compound are found with the organolanthanide complex $\{[C_5H_3(SiMe_3)_2]_2Ce(\mu\text{-}OC)W(CO)(Cp)(\mu\text{-}CO)\}_2$,[39] which contains two bridging carbonyl groups and a single terminal carbonyl group on the transition-metal center. Interestingly, the two terminal groups lie on opposite sides of the ring, giving it a chair conformation, whereas the terminal carbonyls lie on the same side of the ring in the Ca–Cr complex, and the ring adopts a shallow dish shape (Figure 2).

Limitations on Substrates. The requirements for the formation of isolable heterometallic complexes with the alkaline earths are not completely satisfied by ensuring that ligand exchange is degenerate or unfavorable. If the transition-metal substrate is only weakly basic, isolation of a stable complex may not be possible. No reaction is observed between $Cp^{*}_{2}Ca$ and $Cp^{*}_{2}HfH_2$, for example, and a mixture of $Cp^{*}_{2}Ca$ and $Cp^{*}_{2}HfHCl$ in toluene displays only slight shifts in the ^1H NMR resonances; no bimetallic species has been isolated.

Another complication can arise from the moderately strong reducing ability of the Cp^{*-} anion. As an example, $Cp^{*}_{2}Ca$ will react with Cp_2TiCl_2 in toluene to produce Ti(III) species.[22] If a high-valent transition-metal complex is to be used, such reduction can be avoided by using second- and third-row transition-metal species for which reduction is more difficult (as with the Zr(IV) and Hf(IV) compounds) or by employing electronically saturated compounds that will resist further reduction (as with the Cr carbonyl).

Conclusions

The inherent Lewis acidity of organoalkaline-earth metals can be exploited to form heterometallic complexes with transition-metal-based nucleophiles. The kinetic lability of the alkaline-earth species is not a severe impediment to their formation, if the ligands are chosen so that exchange would either be degenerate or would require the alkaline-earth center to bind to unfavorably "soft" ligands. Elaboration of the design principles outlined here should make possible the use of a wider variety of ligands and permit the construction of heterometallic complexes with the late-transition or posttransition elements.

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Supplementary Material Available: A fully numbered diagram of $Cp^{*}_{2}HfCl(\mu\text{-}Cl)CaCp^{*}_{2}$ and tables of bond distances and angles and anisotropic thermal parameters (6 pages). Ordering information is given on any current masthead page.

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(33) Crystals of $[Cp^{*}_{2}Ca(\mu\text{-}OC)_2(OC)Cr(mes)]_2\cdot 2(toluene)$ were grown from toluene but proved to be poorly diffracting with broad peaks. The best of these was found to be monoclinic, space group $P2_1/n$ (alternate setting of $P2_1/c$, No. 14), with a = 14.965 (5) Å, b = 32.966 (9) Å, c = 15.674 (4) Å, β = 103.68 (2)°, and D(calcd) = 1.165 g cm^{-3} for $Z = 4$. Of the 5579 unique reflections that were collected at 20 °C, only 2633 were observed ($I > 3\sigma(I)$). Although the structure appears well-behaved, the R's for averaging (0.18) and final residuals ($R = 0.084$; $R_w = 0.095$) indicate that there are still significant problems. Crystal instability, possibly due to loss of toluene, and evident disorder in one of the toluene molecules are among these, but there may be other disorder or twinning problems that are not as obvious. In any case, the general structure of the complex is unambiguous, although details of bond distances and angles cannot be pressed.

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