reaction times (about 5 h at −10 °C). Contrary to the Co^{II}-catalyzed acylation, both functionalized R′ groups from the dialkylzinc compounds ZnR'_2 are transferred in these allylation reactions (see products **11**–**13** of Scheme 2). In addition, allylic phosphates as well as allylic chlorides react, and with the same high stereoselectivity. Thus the reaction of $Pent_2Zn$ with diethyl cinnamylphosphate (THF, −10 °C, 0.5 h) furnishes the S_N2 allylated product (*E*)-1-phenyloctene (88% yield, 100% *E*, 100% S_N2 substitution). Organozinc reagents also undergo coupling reactions with benzylic bromides. In the reaction of benzyl bromide with 4-acetoxybutylzinc iodide in the presence of $CoBr_2$ (10 mol%) in THF:NMP (1:1) at −10 °C for 5 h, 5-phenylpentyl acetate is isolated in 60% yield.

In conclusion, we have described a new and efficient cobalt(II)- and iron(III)-catalyzed acylation, which provides a general synthesis of polyfunctional ketones. Remarkably the cobalt(II)-catalyzed allylation provides exclusively S_N2 products with complete retention of the double bond geometry. Further studies involving cobalt(II)- and iron(III)-catalyzed reactions of organozinc compounds are underway.

Experimental Procedure

Typical syntheses are as follows:

Bis(4-pivaloxybutyl)zinc: A 50 mL, three-necked flask was charged with 4-iodobutyl pivalate (8.52 g, 30 mmol), CuI (60 mg, 0.3 mol%), and Et_2Zn (4.5 mL, 40 mmol, 1.3 equiv). The reaction mixture was stirred at 55 °C for 14 h. The volatiles were removed under vacuum (55 °C, 0.1 mmHg, 2 h). After addition of decane (10 mL), all traces of Et_2Zn were removed under high vacuum (1 h). This last operation was performed twice. The resulting zinc reagent was diluted in ether (10 mL) and was ready to use.

5-Oxododecyl pivalate (**4**): A 50 mL three-necked flask was charged with $CoBr_2$ (218 mg, 1 mmol) in NMP (4 mL) and ether (2 mL). The reaction mixture was cooled to −10 °C and *n*-octanoyl chloride (1.62 g, 10 mmol) was added followed by bis(4-pivaloxy-butyl)zinc (4 mL of the solution prepared as described above, 10 mmol). The resulting deep blue solution was stirred for 0.5 h at −10 °C and worked up as usual. After evaporation of the solvents, the crude residue was purified by flash chromatography (hexane:ether = 95:5), providing **4** (2.2 g, 78% yield) as a colorless oil.

6-Heptenyl pivalate (**12**): A 50 mL three-necked flask was charged with $CoBr_2$ (218 mg, 1 mmol) in THF (5 mL). The reaction mixture was cooled to −10 °C, and allyl bromide (2.42 g, 20 mmol) followed by bis(4-pivaloxybutyl)zinc (4 mL, 10 mmol) was added. The resulting solution was stirred for 5 h at this temperature and worked up as usual to afford, after flash chromatography, 3.32 g of the ester **12** (16.8 mmol, 84% yield).

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Hexakis(but-3-ynyl)benzene**

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Interest in polyalkyne compounds has increased over the last few years[1–5] due to their use as building blocks for the construction of extended molecular frameworks needed in supramolecular assemblies[1a] and molecular electronic devices.[2] For instance, Diederich et al. have synthesized various polyalkynes with exotic shapes,[3] and Bunz et al. have devised a strategy to couple alkyne-derived transition metal complexes to form linear arrays and grids.[4] Vollhardt et al. have reported on two appealing compounds in the hexaalkynylbenzene family, hexaethynyl-[5a] and hexabutadiynylbenzene.[5b] However, little is known concerning hexaalkynylbenzenes in which methylene units separate the benzene ring and the alkyne functions.[6]

The $FeCp^+$-induced formation of multiple C–C bonds in Equation (a) proceeds readily with alkyl, allyl, and benzyl

$$[\mathrm{FeCp(C_6Me_6)}]^+\mathrm{PF_6^-} \xrightarrow[\text{base}]{\text{RX}} [\mathrm{FeCpC_6(CH_2R)_6}]^+\mathrm{PF_6^-} \qquad (a)$$

halides;[7] however, this reaction does not allow the direct introduction of alkynes. Indeed, triple bonds are not compatible with the required base. For instance, the reactions of propargyl bromide with KOH in DME or KO*t*Bu in THF with complexes of the series $[\mathrm{FeCp(C_6H_{6-n}Me_n)}]^+\mathrm{PF_6^-}$ give polymers. Since the $FeCp^+$-induced hexaallylation of C_6Me_6 proceeds readily,[8] we attempted to use this indirect route to synthesize hexakis(but-3-ynyl)benzene. We now report on the synthesis, structure, and reactions of this compound.

The reaction of excess allyl bromide and KO*t*Bu in THF with $[\mathrm{FeCp(C_6Me_6)}]^+\mathrm{PF_6^-}$ (**1**) gave the hexaallylated complex $[\mathrm{FeCp\{C_6(CH_2CH_2CH{=}CH_2)_6\}}]^+\mathrm{PF_6^-}$ (**2**) [Eq. (a), R = $CH_2CH{=}CH_2$; Scheme 1). Although **2** can be transformed into

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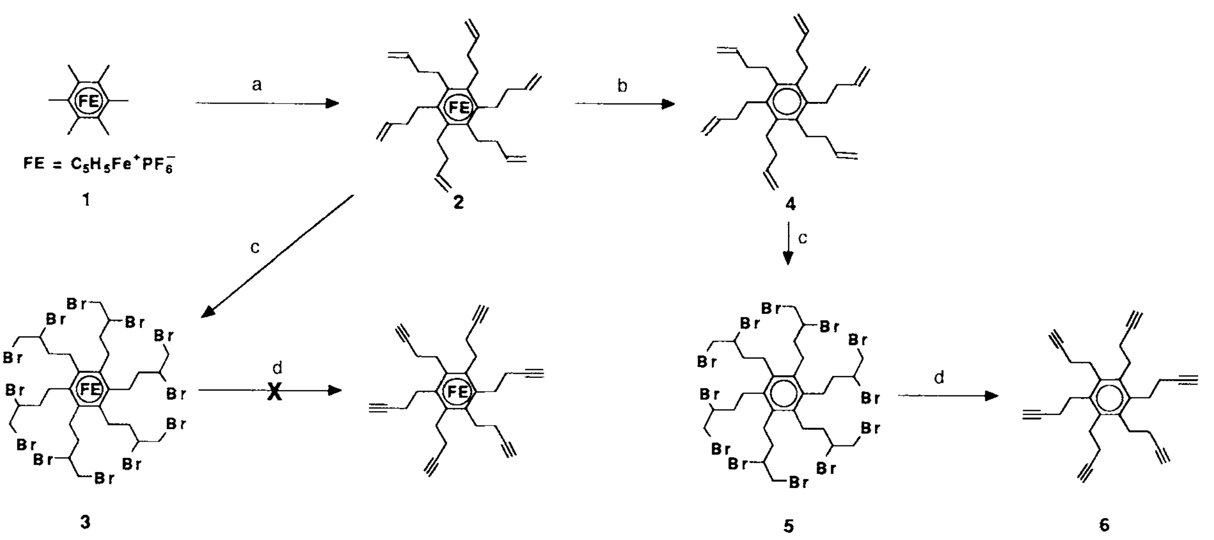


Scheme 1. Synthesis of **6**: a) $CH_2{=}CHBr$, KOH, 40 °C; b) $h\nu_{(vis)}$, CH_3CN, PPh_3, room temperature; c) Br_2 in CH_2Cl_2, room temperature; d) $NaNH_2$ in NH_3, −33 °C.

its dodecabromo derivative **3**,[8] we found that the dehydrohalogenation of the latter using $NaNH_2$ in liquid NH_3 gave a product whose ^1H and ^{13}C NMR spectra show the presence of double bonds and of several kinds of triple bonds, presumably resulting from isomerization under the reaction conditions.[9a] The analogous dehydrohalogenation of the metal-free analogue **5** was successful. Photochemical decomplexation of **2** using visible light in CH_2Cl_2 or CH_3CN quantitatively gave **4**.[8] Reaction of Br_2 with **4** in CH_2Cl_2 provided the new insoluble dodecabromo derivative **5** (negative-ion FAB mass spectrum: $[M + Br^-]$), which is also characterized by its correct elemental analysis. Dehydrohalogenation of **5** proceeded by reaction with $NaNH_2$ in liquid NH_3[9] and gave hexakis(but-3-ynyl)benzene (**6**) in 74–81% yield as a white powder (Scheme 1); this synthesis was reproduced many times.

In the pure state, **6** is air-stable at ambient temperature for weeks and thermally stable. The ^1H NMR spectrum of **6** does not change upon heating in [D$_8$]toluene at 100–110 °C for 18 h. The slow evaporation of a saturated THF solution of **6** provides large transparent crystals. The X-ray structure determination reveals crystallographic $\bar{1}$ symmetry for **6**.[10] The $C{\equiv}CCH_2$ units are almost linear, with angles between 176.2(1) and 177.9(1)°. The branches are alternating above and below the plane of the aromatic ring (Fig. 1). Two of the three symmetrically independent substituents have a stretched conformation (*trans* with regard to the $CH_2{-}CH_2$ bond, with torsion angles of 168.3(1) and 163.6(1)°); the third substituent has a folded conformation (*gauche* arrangement, with a torsion angle of 57.1(2)°). The C-C-C angles of the latter are larger than those of the two other branches. All equivalent C–C bonds have almost identical lengths within the limits of their estimated standard deviations.

Force-field calculations on **6** show the all-*trans* (D_{3d}) conformation to be the most stable and 11.3 kJ mol^{-1} lower in energy than the C_i arrangement found in the crystal structure (Fig. 1; four *trans* and two *gauche* conformations, Table 1). A decrease in molecular symmetry due to crystal forces is a common phenomenon. Since small energy differences like that calculated here can readily be compensated by lattice energy differences between conformers, the order of stability in the solid state may be reversed.[11]

Reactions of **6** are illustrated in Scheme 2. Addition of BuLi in hexane to **6** in THF immediately provided a white precipitate, which is only poorly soluble in *N,N,N′,′*-tetramethylethylenediamine (TMEDA). Further reactions show that this compound is the hexalithiated derivative **7**. Various electrophiles (MeI, $SiMe_3Cl$, CO_2) were added to a suspension of **7** to furnish the hexasubstituted derivatives **8**–**10** (Scheme 2, Table 2). Hexakis(pent-3-ynyl)benzene (**8**) was obtained in crystalline form in 90% yield by slow evaporation of an ethereal solution of the reaction mixture. The trimethylsilyl derivative **9** was obtained as

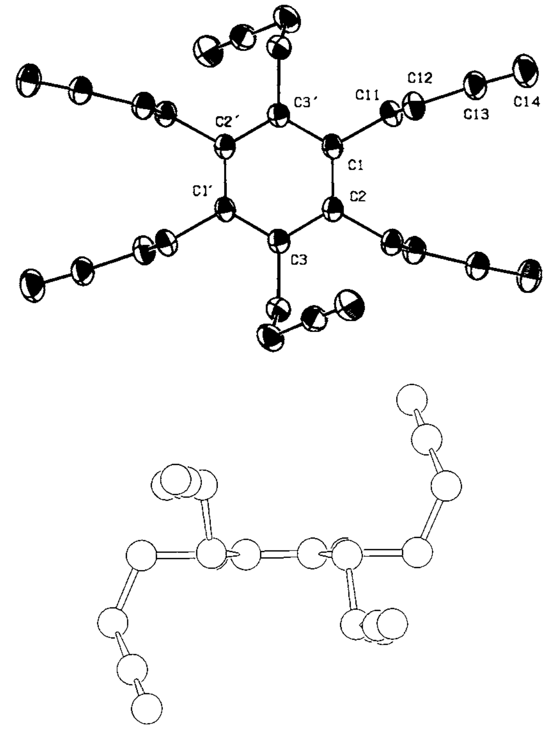


Fig. 1. X-ray crystal structure of **6**. Top: View onto the plane of the benzene ring (ORTEP plot, the ellipsoids are scaled to 30% probability). Bottom: Side view (SCHAKAL plot). Primed atoms are related to the unprimed by the symmetry operation $-x, -y, -z$. Selected distances [Å] and angles [°]: C1–C2 1.408(1), C2–C3 1.404(1), C1–C3 1.405(1), C1–C11 1.515(1), C2–C21 1.518(1), C3–C31 1.518(1), C11–C12 1.541(2), C21–C22 1.541(1), C31–C32 1.545(2), C12–C13 1.461(1), C22–C23 1.464(1), C32–C33, 1.452(2), C13–C14 1.179(2), C23–C24 1.189(2), C33–C34 1.182(2); C1-C11-C12 111.71(8), C2-C21-C22 111.41(8), C3-C31-C32 113.9(1), C11-C12-C13 111.3(1), C21-C22-C23 112.67(9), C31-C32-C33 115.0(1), C12-C13-C14 176.2(1), C22-C23-C24 177.2(1), C32-C33-C34 177.9(1).

Table 1. Conformations of **6** obtained by force-field calculations.

Conformation	Symmetry	E [kJ mol^{-1}]	Torsion angle [°]
all-*trans*	D_{3d}	0.0	-
4 × *trans*, 2 × *gauche*	C_i	−11.3	55.7
all-*gauche*	C_{3i}	−23.7	57.2
all-*gauche*	D_3	−27.4	

a white powder in 97% yield. The carboxylic acid **10** was isolated after hydrolysis and acidic workup. Reaction of **6** with Lappert's reagent Me_2NSnMe_3[12] afforded the hexastannyl derivative **11** as a white powder in 95% yield after standard purification.

The six triple bonds of **6** were π-complexed by $[Co_2(CO)_6]$[1b,c] by reaction with $[Co_2(CO)_8]$ in pentane. The

Table 2. Selected spectroscopic and physical data for compounds **6**, **8**–**13**.

6: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.90 (t, J = 8 Hz, 12 H, CH_2C_{Ar}), 2.33 (td, J = 8, 2 Hz, 12 H, CH_2CC), 2.05 (t, J = 2 Hz, 6 H, CCH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 136.2 (C_{Ar}, s), 83.5 (CCH, dm, ^2J(C,H) = 50 Hz), 69.4 (CCH, dt, ^1J(C,H) = 248 Hz, ^3J(C,H) = 4 Hz), 28.9 (CH_2C_{Ar}, t, ^1J(C,H) = 129 Hz), 20.4 (CH_2CC, t, ^1J(C,H) = 132 Hz)

8: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.81 (pseudo-t, J = 8 Hz, 12 H, CH_2C_{Ar}), 2.24 (br., 12 H, CH_2CC), 1.81 (s, 18 H, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 136.2 (C_{Ar}), 78.7 (CCMe), 76.4 (CCMe), 29.4 (CH_2C_{Ar}), 20.8 (CH_2CC), 3.7 (Me); Anal. calcd. for $C_{36}H_{42}$: 91.08 C, 8.92 H; found: 91.24 C, 8.90 H; m.p. 172 °C

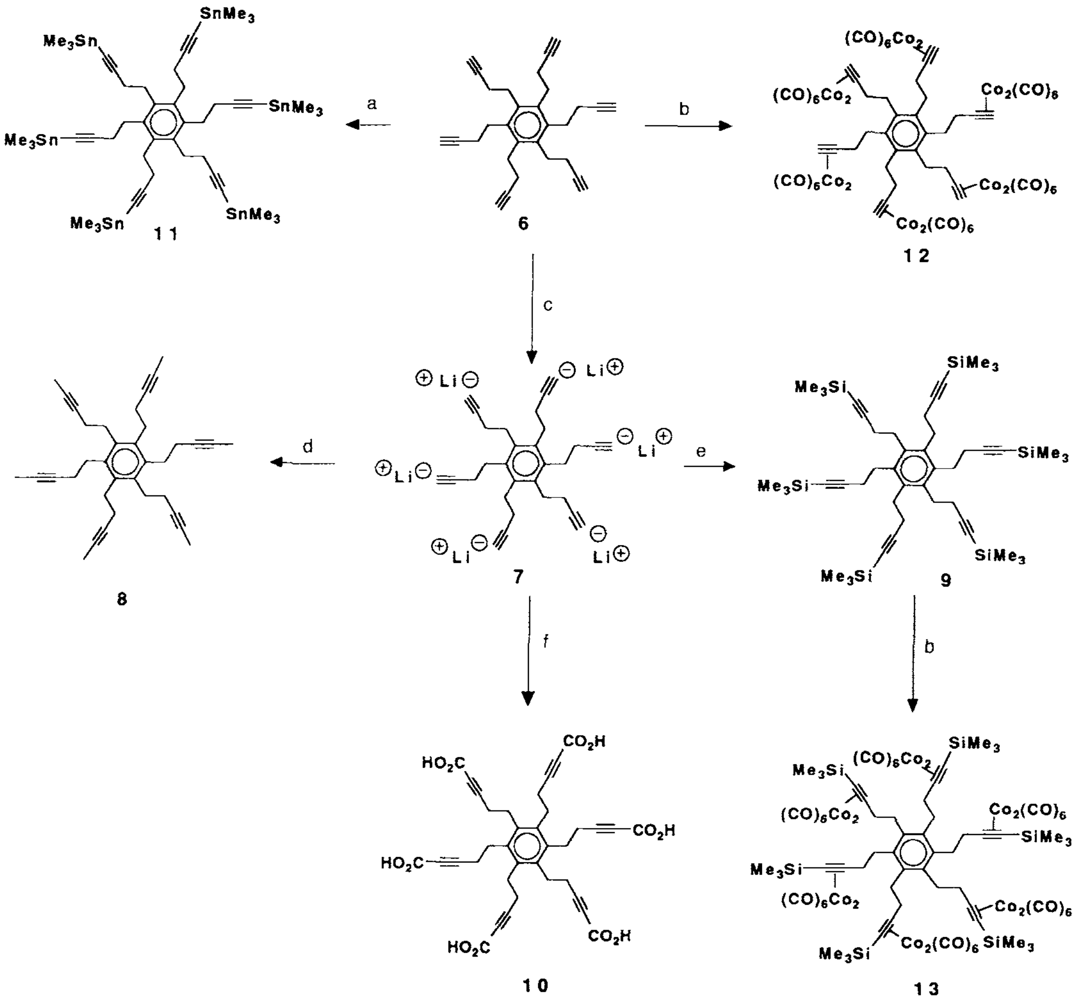
9: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.86 (pseudo-t, J = 8.1 Hz, 12 H, CH_2C_{Ar}), 2.34 (pseudo-t, J = 8.1 Hz, 12 H, CH_2CC), 1.50 (s, 2 H, H_2O), 0.17 (s, 54 H, $SiMe_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 136.3 (C_{Ar}), 106.4 (CCSi), 85.4 (CCSi), 29.1 (CH_2C_{Ar}), 21.8 (CH_2CC), 0.2 ($SiMe_3$); Anal. calcd. for $C_{48}H_{80}SiO$: 68.50 C, 9.58 H; found: 68.93 C, 9.58 H; m.p. 191–192 °C

10: ^{1}H NMR (250 MHz, [D_6]acetone): δ = 7.8 (br., 6 H, CO_2H), 3.11 (pseudo-t, J = 7.5 Hz, 12 H, CH_2C_{Ar}), 2.63 (pseudo-t, J = 7.5 Hz, 12 H, CH_2CC); ^{13}C NMR (62.9 MHz, [D_6]acetone): δ = 154.6 (CO_2H), 137.0 (C_{Ar}), 88.6 ($CCCO_2H$), 75.0 ($CCCO_2H$), 28.3 (CH_2C_{Ar}), 20.5 (CH_2CC); IR (film): $\tilde{\nu}$ = 2230 (C≡C), 1680 (CO) cm^{-1}

11: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.87 (pseudo-t, J = 7.3 Hz, 12 H, CH_2C_{Ar}), 2.35 (br., 12 H, CH_2CC), 0.29 (s, 54 H, Sn Me_3, ^{119}Sn satellites: J(Sn,H) = 59.0 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 136.3 (C_{Ar}), 110.0 (CCSn), 83.2 (CCSn), 29.5 (CH_2C_{Ar}), 22.1 (CH_2CC), −7.7 ($SnMe_3$, Sn satellites of various isotopes); IR (film): $\tilde{\nu}$ = 214 (C≡C) cm^{-1}

12: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.19 (s, 6H, CCH), 3.07 and 2.98 (br., 12 H each, CH_2CH_2); IR (film): $\tilde{\nu}$ = 2090, 2055, 2022 cm^{-1}; Anal. calcd. for $C_{66}H_{30}Co_{12}O_{36}$: 37.64 C, 1.44 H, 33.58 Co; found: 37.64 C, 1.68 H, 33.04 Co

13: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.22 and 3.10 (br., 12 H each, CH_2CH_2), 0.26 (s, 54 H, $SiMe_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 200.4 (CO), 137.4 (C_{Ar}), 110.3 and 80.4 (CC), 37.2 and 31.4 (CH_2CH_2), 0.5 ($SiMe_3$); IR (film): $\tilde{\nu}$ = 2085, 2070, 2045, 2020 cm^{-1}



Scheme 2. Reactions of **6**: a) Me_2NSnMe_3; b) $[Co_2(CO)_8]$, pentane, room temperature; c) *n*BuLi, THF, room temperature; d) MeI, THF, room temperature; e) Me_3SiCl, THF, room temperature; f) CO_2, THF then aq. HCl, room temperature.

reaction was accompanied by violent evolution of CO and after a few minutes the red compound **12** formed. This compound is almost insoluble in standard solvents but gave satisfactory elemental analysis and a clean ^{1}H NMR spectrum (after 2000 scans (!), 250 MHz, $CDCl_3$). In contrast, analogue **13**, which has six $SiMe_3$ groups, is readily soluble in various solvents and was easily characterized by ^{1}H and ^{13}C NMR spectroscopy (Scheme 2, Table 2).

In conclusion, hexakis(butynyl)benzene (**6**), now easily and reproducibly accessible, is a very stable compound which shows a well-defined conformation in the solid state and a rich synthetic chemistry. Various hexaalkynylbenzenes, including functionalized derivatives and potentially useful synthetic intermediates, can be obtained from hexamethylbenzene in high yield.

Experimental Procedure

5: To a cold solution (-80 °C) of hexakis(butenyl)benzene (1.00 g, 2.48 mmol) in 50 mL of CH_2Cl_2 was added dropwise Br_2 (0.8 mL, 2.5 g, 15.6 mmol). The solution was stirred for 30 min at room temperature before the product was filtered off, washed with pentane (3 × 10 mL), and dried in vacuo. This gave 3.04–3.21 g (90–95%) of **5** as a white powder.

6: At -70 °C, 100 mL of NH_3 was condensed into a large Schlenk tube. After addition of a small amount of $Fe(NO_3)_3 \cdot 9H_2O$, Na (6.10 g, 265 mmol) was added in small portions. When H_2 evolution had ceased (the slurry was now gray), 3.00 g of **5** was added. The temperature was first raised to -60 °C (16 h), then to -35 °C (5 h). The mixture was hydrolyzed by addition of NH_4Cl (14.40 g, 269 mmol) and NH_3 was evaporated under reduced pressure. After addition of aq. HCl (pH < 4), the product was extracted with CH_2Cl_2. The organic layers were washed with water, dried over Na_2SO_4, filtered, and concentrated to dryness. Flash chromatography (Al_2O_3, 8 × 2 cm, Et_2O) yielded 640–700 mg (74–81%) of **6** as a white powder.

7: A solution of BuLi in hexane (0.92 mL, 1.6 M, 1.47 mmol) was slowly added to a cold (-70 °C) solution of **6** (95.3 mg, 0.244 mmol) in 20 mL of THF. After 15 min lithiation was complete and a white precipitate had formed. This suspension was used in subsequent reactions.

9: A twofold excess of Me_3SiCl was added to the suspension of **7** prepared as described above. The precipitate dissolved immediately. The solvent was evaporated and the product was dissolved in Et_2O. The organic phase was washed twice with water, dried over Na_2SO_4, and filtered. After evaporation of the solvent, the product was purified by flash chromatography (Al_2O_3, 5 × 2 cm, Et_2O). The white powder (97%) contained 1 equiv of water and was very soluble in Et_2O, THF, and CH_2Cl_2, but only sparingly soluble in pentane.

10: A stream of dry CO_2 was bubbled through a suspension of **7** first at -70 °C, later at room temperature. After evaporation of the solvent, water was added, the suspension was filtered, and the solution was acidified with aq. HCl. The solid that had formed was filtered, dissolved in Et_2O, and precipitated with pentane. The product (70%) was filtered and dried. It was soluble in Et_2O, acetone, and aq. NaOH, but only sparingly soluble in pentane and CH_2Cl_2.

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[10] Crystal structure determination of **6** ($C_{30}H_{30}$): Enraf-Nonius CAD4 diffractometer, $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å), $T = -45$ °C, crystal size $0.30 \times 0.40 \times 0.60$ mm^3; $M_r = 390.57$; $a = 8.141(4)$, $b = 11.512(3)$, $c = 12.812(4)$ Å, $\alpha = 96.04(3)°$, $V = 1194(1)$ Å^3, monoclinic, space group $P2_1/n$ (no. 14), $Z = 2$, $\rho_{calcd} = 1.088$ g cm^{-3}, $\mu = 4.27$ cm^{-1}, $F_{000} = 420.0$; 2419 reflections were measured in the range $5 \leq \theta \leq 70°$ (ω-scan), 2034 of which with $I > 3\sigma(I)$; 2011 independent reflections with $I > 1\sigma(I)$ were used for 197 parameters; solution and refinement of the structure with SDP [13]: $R(F) = 0.054$, $R_w(F) = 0.081$, GOF = 2.655, residual electron density 0.15 e Å^3. Non-hydrogen atoms were refined anisotropically, hydrogen atoms istropically. No correction for absorption; secondary extinction coefficient 1.06×10^{-5} [14]. A weighting scheme $1/\sigma^2(F_0)$ was applied to all reflections. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-39. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

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The Novel Encapsulation of Transition Metals in a Bioctahedral Rare Earth Metal Cluster: $Cs_2La_{10}I_{17}Co_2$

Michael Lulei, Paul A. Maggard, and
John D. Corbett*

*Dedicated to Professor Hans Georg von Schnering
on the occasion of his 65th birthday*

The rare earth metal halides form a remarkable variety of highly reduced phases that contain metal clusters.[1,2] The great majority of these clusters are derived from octahedral units M_6 that are centered by an interstitial atom and are bridged over

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