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Synthesis and X-ray Crystallographic Characterization of an Asymmetric Organoyttrium Halide Dimer: $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$

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YCl_3 reacts with 2 equiv of KC_5Me_5 in THF at room temperature to form $(C_5Me_5)_2YCl_2K(THF)_2$, I, in 60–70% yield. I loses THF under vacuum. When I is heated to 285 °C at 4×10^{-5} torr, $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_2)_2$, II, sublimes in 70–80% yield. Upon resublimation over 18 h with a 170–250 °C thermal gradient, II crystallizes in space group $P2_1/c$ with unit cell dimensions a = 10.920 (3) Å, b = 26.759 (9) Å, c = 14.560 (4) Å, β = 109.49 (7)°, and Z = 4 (dimers) for D_{calcd} = 1.31 g cm^{-3}. Least-squares refinement on the basis of 1677 reflections led to a final R value of 0.063. II has an asymmetrical structure in which one yttrium atom is attached to a nonbridging chloride atom at a distance of 2.579 (6) Å and to a bridging chloride at a distance of 2.776 (5) Å. The other yttrium atom is attached to the bridging chloride at a distance of 2.640 (5) Å. The Y–(μ-Cl)–Y′ angle is 162.8 (2)°. A single C_5Me_5 resonance is observed in the ^1H NMR spectrum at room temperature, but at low temperature a 1:1:2 pattern consistent with an asymmetric structure is observed.

Our recent synthesis and structural characterization of the hydride dimer $[(C_5Me_5)_2SmH]_2$[2] and the recent data reported on the methyl and hydride complexes $[(C_5Me_5)_2LuZ]_n$[3] (Z = CH_3, H; n = 1, 2) raise some interesting questions regarding the structures of $[(C_5Me_5)_2LnX]_n$ complexes in general (Ln = a lanthanide metal or yttrium; X = halide, hydride, alkyl, etc.). $[(C_5Me_5)_2SmH]_2$ has a symmetrical structure in which both of the bent metallocene subunits $(C_5Me_5)_2Sm$ are equivalent.[2] The hydrogen atoms were not located in the X-ray study but are likely to reside in symmetrically bridging positions like the hydrogen bridges in $[(C_5Me_5)_2ThH(\mu\text{-}H)]_2$.[4] $[(C_5Me_5)_2LuZ]_n$ complexes, on the other hand, are reported to have the asymmetric structure $[(C_5Me_5)_2Lu(\mu\text{-}Z)LuZ(C_5Me_5)_2]$ at low temperature in solution based on NMR spectroscopy.[3] Unpublished X-ray data have been cited which indicate that the methyl complex has this structure in the solid state.[3] The dimeric C_5Me_5 lutetium structures differ substantially from the crystallographically established symmetrical structures of the C_5H_5 and $CH_3C_5H_4$ complexes $[(C_5H_5)_2Yb(\mu\text{-}CH_3)]_2$,[5] $[(C_5H_5)_2Y(\mu\text{-}CH_3)]_2$,[5] and $[(CH_3C_5H_4)_2Y(THF)(\mu\text{-}H)]_2$.[6] Since the chloride ligand is much easier to locate in an X-ray study than a hydride and since it has none of the bonding ambiguities inherent in a methyl bridge (M–C–M bonding or M–C–H–M bonding[5]), we have examined the structure of a bis(pentamethylcyclopentadienyl) chloride complex, $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$. Yttrium was chosen for this study because, as discussed previously,[7] it has been observed in the past to be chemically and structurally similar to the late lanthanides[5-9] and it has particularly favorable NMR properties. This study has provided the first fully refinable data on an asymmetrically bridged bis(ring) halide complex of metals of this type.[10]

Experimental Section

The complexes described below are extremely air and moisture sensitive. Therefore, all syntheses and subsequent manipulations of these compounds were conducted with the rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques. Since some of the complexes rapidly form adducts with THF, a rigorously ether-free glovebox was often necessary for handling these compounds.

Materials. Toluene and THF were distilled from potassium benzophenone ketyl. THF-d_8, toluene-d_8, and benzene-d_6 were vacuum transferred from potassium benzophenone ketyl. Anhydrous yttrium trichloride was prepared from the hydrate (Research Chemicals, Phoenix, AZ) by the method of Taylor and Carter.[12] KC_5Me_5 was obtained from C_5Me_5H (Aldrich) using KH in THF.

Physical Measurements. Infrared spectra were obtained as previously described.[7] ^1H NMR spectra were recorded by using a Bruker 250-MHz spectrometer and were referenced to residual β-methylene protons in C_4D_8O (δ 1.72), to residual aryl protons in C_6D_6 (δ 7.15), or to residual methyl protons in $C_6D_5CD_3$ (δ 2.30). All shifts are reported in parts per million. Complete elemental analyses were obtained from Analytische Laboratorien, Engelskirchen, West Germany. Complexometric analyses were obtained as previously described.[13]

$(C_5Me_5)_2YCl_2K(THF)_2$, I. In the glovebox, solid KC_5Me_5 (4.61 g, 26.4 mmol) was added to a slurry of YCl_3 (2.58 g, 13.2 mmol) in 120 mL of THF in a 250-mL flask. The thick milky gray suspension was stirred for 12 h at room temperature, during which time the gelatinous white solids appeared to become more granular. These solids were filtered from the solution, and THF

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was removed from the filtrate by rotary evaporation to give a white powder. This powder was extracted with two 50-mL portions of toluene (to remove $(C_5Me_5)_2YCl(THF)$ as described in the next section) and then dried under vacuum to remove residual toluene. The dry powder was redissolved in THF and filtered to remove a small amount of THF-insoluble material. THF was removed from the solution by rotary evaporation to give $(C_5Me_5)_2YCl_2K(THF)_2$, I, (6.5 g, 69%) as a bright white powder: ^1H NMR (C_4D_8O) δ 1.89 (s, 30 H, C_5Me_5), 1.77 (t, 4–5 H, THF), 3.61 (t, 4–5 H, THF); IR (KBr, cm^{-1}) 2975 s, 2898 s, 2870 s, 2859 s, 2716 w, 1493 w, 1485 w, 1440 s, 1433 s, 1373 m, 1053 s, 1019 m, 909 m, 892 m, 865 m, 803 w, 797 w. Anal. Calcd for $C_{28}H_{46}O_2Cl_2KY$ (disolvate): C, 54.81; H, 7.55; O, 5.21; Cl, 11.55; K, 6.37; Y, 14.49. Found: C, 54.50; H, 7.34; K. 6.50 (Analytische Laboratorien); Y, 14.53 (complexometric). The amount of THF present depends on how long the sample is dried under vacuum. Analytical data on the monosolvate $(C_5Me_5)_2YCl_2K(THF)$ have also been obtained from preparations of I. Calcd for $C_{24}H_{38}OCl_2KY$ (monosolvate): C, 53.24; H, 7.07; O, 2.95; Cl, 13.09; Y, 16.42. Found: Y, 16.25; Cl, 13.24.

$(C_5Me_5)_2YCl$ (THF). Solvent was removed from the toluene extract described above to leave a yellow solid (0.665 g). Examination of the ^1H NMR spectrum (C_6D_6) of the extracted solid showed a major peak at δ 2.02 corresponding to the crystallographically characterized $(C_5Me_5)_2YCl(THF)$[14] as well as a complex pattern of at least nine less intense peaks in the C_5Me_5 region. The yield of $(C_5Me_5)_2YCl(THF)$ in this reaction was 7%.

$[(C_5Me_5)_2YCl]_2$, II. I (1.5 g, 2.44 mmol) as $(C_5Me_5)_2YCl_2K(THF)_2$ was placed in the bottom bulb of a sublimation tube consisting of a 2.5 × 27 cm Pyrex tube which had a constriction 7 cm from the bottom and 24/40 ground glass joint at the top. I was added through a smaller tube inserted into the sublimation tube so that no material contacted the walls in the upper part of the sublimation tube. A stopcock adapter was attached to the tube, and the sample was placed under dynamic vacuum. A tube furnace was placed around the bottom part of the sublimation tube such that at least half of the constricted area was fully heated. Glass wool was placed around the furnace opening. The top of the tube was wrapped with Tygon tubing through which cold water flowed. The pressure rose to 10^{-2} torr initially as the tube was heated to 285 °C but fell to 4×10^{-5} torr after 0.5 h and eventually to 2×10^{-5} torr. Over a period of 24 h at 285 °C, a yellow powder, II (0.747 g, 77%), sublimed: ^1H NMR (C_6D_6, 295 K) δ 2.01 (s, C_5Me_5); no peaks were observed corresponding to THF. Addition of a stoichiometric amount of THF to the NMR sample caused the C_5Me_5 peak to shift downfield to δ 2.02. Peaks due to coordinated THF were centered at δ 3.49 and 1.14. This spectrum was identical with the spectrum in C_6D_6 of several crystals from the same crop that yielded a single crystal of $(C_5Me_5)_2YCl(THF)$ for X-ray diffraction:[14] ^1H NMR ($C_6D_5CD_3$, 295 K) δ 2.21; ^1H NMR ($C_6D_5CD_3$, 203 K, saturated solution) δ 2.54 (30 H), 2.07 (15 H), 1.91 (15 H); IR (KBr, cm^{-1}) 2964 s, 2908 s, 2864 s, 2721 w, 1610 m, 1490 w, 1440 s, 1435 s, 1370 m, 1268 w, 1064 w br, 1023 m, 800 w. Anal. Calcd for $C_{20}H_{30}YCl$: C, 60.84; H, 7.66; Y, 22.52; Cl, 8.98. Found: C, 60.66; H, 7.49; Y, 22.75; Cl, 8.86. The ^1H NMR spectrum (C_4D_8O) of the soluble portion of the white residue remaining in the bottom of the sublimation tube showed a resonance at δ 1.89, corresponding to starting material, as well as a less intense resonance at δ 1.93.

Crystals of II suitable for X-ray diffraction were grown by a second sublimation of this compound sealed in a 6 mm × 90 mm Pyrex tube at 1.5×10^{-5} torr. The lower half of the tube was placed in a tube furnace at 170 °C, and the temperature was raised to 250 °C over a period of 18 h. A ring of translucent yellow prismatic crystals formed just above the top of the tube furnace.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$. Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 25 high angle reflections ($2\theta > 19.5°$) accurately centered on the diffractometer are given in Table I. Data were collected on an Enraf-Nonius CAD-4 diffractometer by the $\theta/2\theta$ scan technique. This method has been previously described.[8] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The space group was uniquely defined by systematic absences to be $P2_1/c$.

Table I. Crystal Data for $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$

compd	$C_{40}H_{60}Y_2Cl_2$
mol wt	789.64
space group	$P2_1/c$
cell constants	
a, Å	10.920 (3)
b, Å	26.759 (9)
c, Å	14.560 (4)
β, deg	109.49 (7)
cell vol, Å^3	4010.73
molecules/unit cell	4
D(calcd), g cm^{-3}	1.31
μ(calcd), cm^{-1}	21.42
radiation	Mo Kα
max cryst dimens, mm	0.15 × 0.15 × 0.25
scan width, deg	0.80 + 0.20 tan θ
std reflctns	600, 080, 004
decay of stds	±2%
reflctns measd	4371
2θ range, deg	2–42
obsd reflctns	1677
no. of parameters varied	197
GOF	1.04
R	0.063
R_w	0.066

Two yttrium atoms were located from electron density maps by direct methods using the MULTAN 80 program system.[15] The subsequent calculation of difference Fourier maps allowed the location of all non-hydrogen atoms. Neutral atom scattering factors for Y, Cl, and C were taken from Cromer and Waber.[16] For H atoms, the values in ref 17 were used. The full-matrix least-squares refinement with isotropic temperature factors using the SHELX program system[18] for all non-hydrogen atoms led to a reliability index of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.087$. Conversion to anisotropic thermal parameters for Y and Cl atoms and further refinement gave $R = 0.073$. Hydrogen atoms were located at positions 1.00 Å away from the bonded carbon atoms, and their parameters were not varied. Additional cycles of refinement gave the final values of $R = 0.063$ and $R_w = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|]^2 = 0.066$ based on 1677 observed reflections ($I > 2\sigma(I)$). The function minimized in the least-squares calculation was $\sum w|\Delta F^2|$ with unit weights. In the last stage of refinement, no parameter shifted by more than 0.01 of its estimated standard deviation. A final difference Fourier synthesis showed one residual peak of 0.54 e/Å^3 near methyl carbon 45 (Me45) and less than 0.47 e/Å^3 elsewhere. No systematic variation of $w(|E_o| - |E_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.

Alternative Synthesis of $[(C_5Me_5)_2YCl]_2$, II. II can also be made from a precursor similar to $(C_5Me_5)_2YCl_2K(THF)_2$ containing lithium rather than potassium. Hence, if the product of the reaction of 2 equiv of LiC_5Me_5 with YCl_3 in THF at reflux is heated to 270 °C at 10^{-4} torr, II also forms. The lithium-based route is not as reliable as the synthesis starting from KC_5Me_5, however. Variations in the success of reactions of C_5Me_5 lanthanide systems due to the precise choice of alkali metal previously have been observed.[19]

Results and Discussion

Synthesis. The primary reaction of YCl_3 with 2 equiv of KC_5Me_5 in THF at room temperature is the formation

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Table II. Final Fractional Coordinates for $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$

atom	*x/a*	*y/b*	*z/c*
Y(1)	0.3243 (2)	−0.14924 (7)	0.5336 (1)
Y(2)	0.6627 (2)	−0.12919 (7)	0.8951 (1)
Cl(1)	0.4693 (4)	−0.1422 (2)	0.7301 (3)
Cl(2)	0.4687 (5)	−0.2190 (2)	0.5023 (4)
Cp(11)	0.350 (2)	−0.0960 (7)	0.387 (1)
Cp(12)	0.263 (2)	−0.0706 (7)	0.414 (1)
Cp(13)	0.327 (2)	−0.0509 (7)	0.509 (1)
Cp(14)	0.455 (2)	−0.0650 (7)	0.533 (1)
Cp(15)	0.476 (2)	−0.0933 (7)	0.461 (1)
Me(11)	0.334 (2)	−0.1218 (9)	0.289 (2)
Me(12)	0.130 (2)	−0.0543 (9)	0.352 (2)
Me(13)	0.266 (2)	−0.0171 (8)	0.565 (2)
Me(14)	0.563 (2)	−0.0437 (8)	0.623 (2)
Me(15)	0.598 (2)	−0.1123 (9)	0.451 (2)
Cp(21)	0.145 (2)	−0.1725 (7)	0.613 (1)
Cp(22)	0.198 (2)	−0.2190 (7)	0.598 (1)
Cp(23)	0.155 (2)	−0.2242 (8)	0.494 (1)
Cp(24)	0.084 (2)	−0.1839 (8)	0.449 (2)
Cp(25)	0.073 (2)	−0.1515 (9)	0.520 (2)
Me(21)	0.151 (2)	−0.1549 (9)	0.712 (2)
Me(22)	0.276 (2)	−0.2554 (8)	0.672 (2)
Me(23)	0.177 (2)	−0.2698 (9)	0.442 (2)
Me(24)	0.007 (2)	−0.1797 (9)	0.339 (2)
Me(25)	−0.015 (3)	−0.107 (1)	0.514 (2)
Cp(31)	0.903 (2)	−0.1601 (8)	0.968 (1)
Cp(32)	0.889 (2)	−0.1373 (7)	0.879 (1)
Cp(33)	0.810 (2)	−0.1695 (7)	0.806 (1)
Cp(34)	0.769 (2)	−0.2083 (7)	0.852 (1)
Cp(35)	0.824 (2)	−0.2022 (9)	0.954 (2)
Me(31)	1.005 (3)	−0.145 (1)	1.068 (2)
Me(32)	0.961 (2)	−0.0923 (9)	0.858 (2)
Me(33)	0.776 (2)	−0.1646 (8)	0.696 (2)
Me(34)	0.678 (2)	−0.2520 (9)	0.806 (2)
Me(35)	0.825 (3)	−0.241 (1)	1.029 (2)
Cp(41)	0.524 (2)	−0.0948 (8)	0.994 (2)
Cp(42)	0.520 (2)	−0.0571 (7)	0.927 (1)
Cp(43)	0.641 (2)	−0.0376 (8)	0.947 (2)
Cp(44)	0.719 (2)	−0.0597 (9)	1.030 (2)
Cp(45)	0.651 (2)	−0.0939 (9)	1.060 (2)
Me(41)	0.415 (3)	−0.129 (1)	1.001 (2)
Me(42)	0.392 (3)	−0.039 (1)	0.847 (2)
Me(43)	0.678 (3)	0.007 (1)	0.897 (2)
Me(44)	0.862 (3)	−0.040 (1)	1.091 (2)
Me(45)	0.703 (3)	−0.124 (1)	1.154 (2)

of $(C_5Me_5)_2YCl_2K(THF)_2$, I, which is isolated in 60–70% yield. A variety of $(C_5Me_5)_2LnX_2M(THF)_2$ complexes (where Ln = lanthanide metal, X = halide, and M = alkali metal) are known.[9,20–23] $(C_5Me_5)_2YCl(THF)$,[14] which is isolated in 7% yield, is the major byproduct of this reaction, but numerous other byproducts also form in small amounts.

The THF molecules in I are labile and can be removed under vacuum. If I is heated under vacuum, complete removal of THF is possible. When I is heated to 285 °C under vacuum, a THF-free, KCl-free product analyzing as $[(C_5Me_5)_2YCl]_2$, II, sublimes. Slow resublimation of II using a thermal gradient generates single crystals suitable for X-ray diffraction.

Crystallographic Studies. An X-ray diffraction study of II was carried out to determine if it had a dimeric structure in the solid state and if the dimer were symmetric or not. As shown in Figure 1, the complex crystallizes as an asymmetrical dimer. Bond distances and angles are presented in Tables III and IV, respectively.

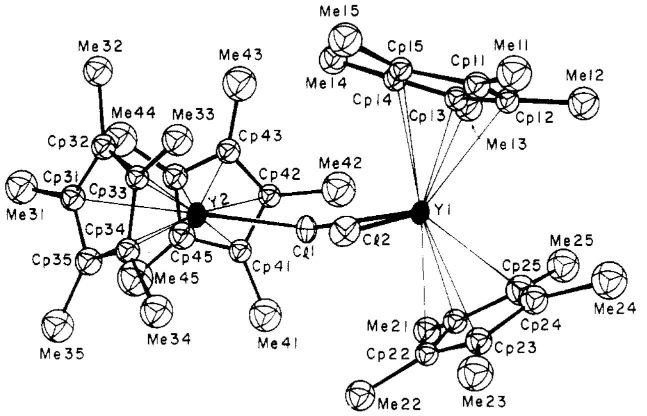

Figure 1. ORTEP plot of the molecular structure of $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$ with yttrium atoms darkened.

Table III. Bond Lengths (Å) for $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$

Y(1)-Cl(1)	2.776 (5)	Y(1)-Cl(2)	2.579 (6)
Y(1)-Cp(11)	2.66 (2)	Y(1)-Cp(12)	2.67 (2)
Y(1)-Cp(13)	2.66 (2)	Y(1)-Cp(14)	2.67 (2)
Y(1)-Cp(15)	2.69 (2)	Y(1)-Cp(21)	2.66 (2)
Y(1)-Cp(22)	2.67 (2)	Y(1)-Cp(23)	2.66 (2)
Y(1)-Cp(24)	2.66 (2)	Y(1)-Cp(25)	2.68 (2)
Y(2)-Cl(1)	2.640 (5)	Y(2)-Cp(31)	2.62 (2)
Y(2)-Cp(32)	2.56 (2)	Y(2)-Cp(33)	2.61 (2)
Y(2)-Cp(34)	2.59 (2)	Y(2)-Cp(35)	2.58 (2)
Y(2)-Cp(41)	2.58 (2)	Y(2)-Cp(42)	2.61 (2)
Y(2)-Cp(43)	2.60 (2)	Y(2)-Cp(44)	2.63 (2)
Y(2)-Cp(45)	2.62 (2)	Cp(11)-Cp(12)	1.33 (2)
Cp(11)-Cp(15)	1.44 (2)	Cp(11)-Me(11)	1.54 (3)
Cp(12)-Cp(13)	1.42 (2)	Cp(12)-Me(12)	1.50 (3)
Cp(13)-Cp(14)	1.37 (2)	Cp(13)-Me(13)	1.51 (3)
Cp(14)-Cp(15)	1.38 (2)	Cp(14)-Me(14)	1.55 (3)
Cp(15)-Me(15)	1.48 (3)	Cp(21)-Cp(22)	1.42 (2)
Cp(21)-Cp(25)	1.43 (3)	Cp(21)-Me(21)	1.51 (3)
Cp(22)-Cp(23)	1.43 (2)	Cp(22)-Me(22)	1.49 (3)
Cp(23)-Cp(24)	1.36 (3)	Cp(23)-Me(23)	1.50 (3)
Cp(24)-Cp(25)	1.39 (3)	Cp(24)-Me(24)	1.54 (3)
Cp(25)-Me(25)	1.51 (3)	Cp(31)-Cp(32)	1.39 (2)
Cp(31)-Cp(35)	1.39 (3)	Cp(31)-Me(31)	1.57 (3)
Cp(32)-Cp(33)	1.42 (2)	Cp(32)-Me(32)	1.52 (3)
Cp(33)-Cp(34)	1.38 (2)	Cp(33)-Me(33)	1.52 (3)
Cp(34)-Cp(35)	1.41 (3)	Cp(34)-Me(34)	1.53 (3)
Cp(35)-Me(35)	1.50 (3)	Cp(41)-Cp(42)	1.40 (3)
Cp(41)-Cp(45)	1.39 (3)	Cp(41)-Me(41)	1.54 (3)
Cp(42)-Cp(43)	1.36 (3)	Cp(42)-Me(42)	1.56 (3)
Cp(43)-Cp(44)	1.36 (3)	Cp(43)-Me(43)	1.52 (3)
Cp(44)-Cp(45)	1.33 (3)	Cp(44)-Me(44)	1.61 (4)
Cp(45)-Me(45)	1.53 (4)	Y(1)-Y(2)	5.354 (2)

Both yttrium atoms are attached to two C_5Me_5 groups with normal bond distances. The relative orientation of the four C_5Me_5 groups in the dimer is approximately like that of a distorted tetrahedron as evidenced by the following torsional angles: ring centroid(1)–Y(1)–Y(2)–ring centroid(3) = −94.9°; centroid(1)–Y(1)–Y(2)–centroid(4) = 74.0°; centroid(2)–Y(1)–Y(2)–centroid(3) = 117.4°; centroid(2)–Y(1)–Y(2)–centroid(4) = −73.8°. This arrangement of C_5Me_5 groups is similar to the tetrahedral orientation of the C_5Me_5 rings in $[(C_5Me_5)_2SmH]_2$,[2] $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$,[24] and $[(C_5Me_5)_2ThH(\mu\text{-}H)]_2$.[4]

One yttrium atom, Y(1), is attached to a terminal, i.e., nonbridging, chloride atom, Cl(2), at a distance of 2.579 (6) Å. This bond length is identical within the error limits to the Y–Cl distances in the two independent molecules in the asymmetric unit of a crystal of monomeric $(C_5Me_5)_2YCl(THF)$,[14] 2.579 (3) and 2.577 (3) Å. As ex-

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Table IV. Bond Angles (deg) for $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$

Cl(1)-Y(1)-Cl(2)	93.4 (2)	Cp(33)-Cp(34)-Me(34)	129 (2)	Cp(22)-Cp(23)-Cp(24)	112 (2)
Cp(12)-Cp(11)-Cp(15)	110 (2)	Cp(31)-Cp(35)-Cp(34)	106 (2)	Cp(24)-Cp(23)-Me(23)	124 (2)
Cp(15)-Cp(11)-Me(11)	120 (2)	Cp(34)-Cp(35)-Me(35)	126 (2)	Cp(23)-Cp(24)-Me(24)	126 (2)
Cp(11)-Cp(12)-Me(12)	128 (2)	Cp(42)-Cp(41)-Me(41)	129 (2)	Cp(21)-Cp(25)-Cp(24)	108 (2)
Cp(12)-Cp(13)-Cp(14)	106 (2)	Cp(41)-Cp(42)-Cp(43)	109 (2)	Cp(24)-Cp(25)-Me(25)	131 (2)
Cp(14)-Cp(13)-Me(13)	128 (2)	Cp(43)-Cp(42)-Me(42)	127 (2)	Cp(32)-Cp(31)-Me(31)	126 (2)
Cp(13)-Cp(14)-Me(14)	123 (2)	Cp(42)-Cp(43)-Me(43)	126 (2)	Cp(31)-Cp(32)-Cp(33)	107 (2)
Cp(11)-Cp(15)-Cp(14)	104 (2)	Cp(43)-Cp(44)-Cp(45)	110 (2)	Cp(33)-Cp(32)-Me(32)	124 (2)
Cp(14)-Cp(15)-Me(15)	131 (2)	Cp(45)-Cp(44)-Me(44)	126 (2)	Cp(32)-Cp(33)-Me(33)	128 (2)
Cp(22)-Cp(21)-Me(21)	122 (2)	Cp(41)-Cp(45)-Me(45)	126 (2)	Cp(33)-Cp(34)-Cp(35)	109 (2)
Cp(21)-Cp(22)-Cp(23)	104 (2)	Y(1)-Cl(1)-Y(2)	162.8 (2)	Cp(35)-Cp(34)-Me(34)	122 (2)
Cp(23)-Cp(22)-Me(22)	127 (2)	Cp(12)-Cp(11)-Me(11)	129 (2)	Cp(31)-Cp(35)-Me(35)	127 (2)
Cp(22)-Cp(23)-Me(23)	124 (2)	Cp(11)-Cp(12)-Cp(13)	108 (2)	Cp(42)-Cp(41)-Cp(45)	105 (2)
Cp(23)-Cp(24)-Cp(25)	108 (2)	Cp(13)-Cp(12)-Me(12)	123 (2)	Cp(45)-Cp(41)-Me(41)	125 (2)
Cp(25)-Cp(24)-Me(24)	125 (2)	Cp(12)-Cp(13)-Me(13)	126 (2)	Cp(41)-Cp(42)-Me(42)	124 (2)
Cp(21)-Cp(25)-Me(25)	120 (2)	Cp(13)-Cp(14)-Cp(15)	111 (2)	Cp(42)-Cp(43)-Cp(44)	108 (2)
Cp(32)-Cp(31)-Cp(35)	110 (2)	Cp(15)-Cp(14)-Me(14)	125 (2)	Cp(44)-Cp(43)-Me(43)	126 (2)
Cp(35)-Cp(31)-Me(31)	124 (2)	Cp(11)-Cp(15)-Me(15)	125 (2)	Cp(43)-Cp(44)-Me(44)	123 (2)
Cp(31)-Cp(32)-Me(32)	129 (2)	Cp(22)-Cp(21)-Cp(25)	109 (2)	Cp(41)-Cp(45)-Cp(44)	109 (2)
Cp(32)-Cp(33)-Cp(34)	108 (2)	Cp(25)-Cp(21)-Me(21)	128 (2)	Cp(44)-Cp(45)-Me(45)	125 (2)
Cp(34)-Cp(33)-Me(33)	124 (2)	Cp(21)-Cp(22)-Me(22)	129 (2)		

pected, the yttrium to bridging chloride distances are longer: Y(1)–Cl(1) = 2.776 (5) Å; Y(2)–Cl(1) = 2.640 (5) Å. These distances differ substantially, however. The bridging chloride atom, Cl(1), is more closely associated with Y(2), the yttrium atom which interacts with only one chloride atom. In fact, the Y(2)–(μ-Cl) distance is closer to the Y(1)–(terminal Cl) distance than to the Y(1)–(μ-Cl) bond length.

Table V allows a comparison of these Y–Cl distances with lanthanide and yttrium chloride bond lengths in a variety of dimeric, monomeric, and Li and Al heterometallic compounds.[9,14,21,23,25–28] Subtraction of the metallic radius[29] from the metal chloride distances provides an "effective chloride radius" which can be used for comparison of all of these data. Although bond lengths will vary depending on the number, nature, and size of the coligands as well as the angles in the bridge systems (which will vary depending on the coligand and the metals involved), some general ranges for effective chloride radii in complexes of this type can be identified. For example, the four values for an effective radius of a chloride attached to these metals in a terminal fashion are in the 1.62–1.70 Å range: 1.63,[9] 1.67,[25] 1.67,[27] and 1.70 Å.[14] The effective chloride radius in cyclopentadienyl homometallic bridged dimers is considerably longer and is in the 1.78–1.80 Å range: 1.78,[11] 1.79,[26] and 1.80 Å.[26] Ln(μ-Cl)$_2$Li complexes have values less than those of homometallic complexes, 1.74[21] and 1.75 Å,[26] and an Yb(μ-Cl)$_2$Al structure has a much larger value, 1.89 Å.[21] In a cyclooctatetraenyl chloride bridged dimer, $[(C_8H_8)Ce(THF)_2(\mu\text{-}Cl)]_2$, each chloride atom displays two different effective radial distances.[28] One distance, 1.82 Å, is close to the values for homometallic cyclopentadienyl dimers; the other distance, 1.90 Å is quite long.

In II, the effective chloride radius of the terminal chloride, Cl(2), 1.70 Å, is in the range of terminal chloride distances found in other complexes. The bridging Cl(1) effective radius relative to Y(2), 1.76 Å, is intermediate between the terminal range and the bridging range. The bridging Cl(1) effective chloride radius relative to Y(1), 1.90 Å, is the longest distance in the table (along with the long distance in $[(C_8H_8)Ce(THF)_2(\mu\text{-}Cl)]_2$).

A discussion[11] of the asymmetry of the two sets of Ce–Cl distances in $[(C_8H_8)Ce(THF)_2(\mu\text{-}Cl)]_2$[28] described this molecule as an example of a dimer on the way to symmetrical fission of two $(C_8H_8)Ce(THF)_2Cl$ monomers. Complex II represents a further step in a hypothetical dimer-to-monomer dissociation process in which one metal chloride bond has already broken and the bridge is asymmetrically oriented in the direction to form two identical $(C_5Me_5)_2YCl$ monomers.

The asymmetry in the cerium complex was attributed to the small size of the chloride with respect to the large metal, cerium.[11] The much greater asymmetry in the structure of II can be attributed to the large size of the C_5Me_5 rings with respect to the small size of yttrium. A symmetrical $(C_5Me_5)_2Y(\mu\text{-}Cl)_2Y(C_5Me_5)_2$ structure for II would be too sterically crowded to be stable.[31] Precedent for steric crowding in bis (C_5Me_5) complexes is available from the examination of the relative orientation of the CH_3 groups (eclipsed or staggered) on the C_5Me_5 rings in the closely related series of the crystallographically characterized molecules $(C_5Me_5)_2Yb(\mu\text{-}I)_2Li(Et_2O)_2$, $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(Et_2O)_2$, and $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2AlCl_2$.[21] This study showed that the methyl groups nearest the bridge halides were often within van der Waals' contacts of the bridge atoms. With large iodide bridging atoms, the steric congestion was greatest and the CH_3 groups of the two rings adopted an eclipsed conformation (less favorable in terms of ring–ring interactions) to avoid the halides as much as possible. Replacement of the $Li(Et_2O)_2$ or $AlCl_2$ unit in these sterically congested complexes with a much larger $(C_5Me_5)_2Ln$ unit may generate a system so sterically overcrowded that the symmetric dibridged dimeric structure cannot form. The asymmetric structure of II and the $(C_5Me_5)_2Lu(\mu\text{-}Z)LuZ(C_5Me_5)_2$ complexes (Z = H, CH_3)[3] can be explained in this way. Obviously, the degree of steric saturation in $[(C_5Me_5)_2LnX]_2$ complexes can be reduced by increasing the size of the metal. Hence, within the lanthanide series by moving from the smaller members later in the series to larger metals at the beginning of the series, the steric overcrowding can be eliminated. At some

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Table V. Yttrium and Lanthanide Metal Chloride Bond Distances (Å) and Angles (deg)

complex	type of chloride terminal (t) or bridging (μ)	(1) M–Cl	(2) general metal radius[a]	(3) "effective chloride radius" (1) – (2)	(4) coordinatn no.	(5) coordinatn no. modified radius[b]	(6) "effective chloride radius" (1) – (5)	M–Cl–M	ref
$\{Yb[CH(SiMe_3)_2]_3Cl\}^-$	t	2.486 (6)	0.858	1.63	4				9
$(C_5Me_5)_2YbCl(Me_2PCH_2PMe_2)$	t	2.532 (3)	0.858	1.67	8	0.985	1.55		27
$[Cp^L{}_2NdCl_2]^-$ [c]	t	2.668 (4)	0.995	1.67	8	1.109	1.56		25
$(C_5Me_5)_2YCl(THF)$	t	2.578 (3)	0.88	1.70	8	1.019	1.56		14
$(C_5Me_5)_2Y(\mu\text{-Cl})\mathit{YCl}(C_5Me_5)_2$	t	2.579 (6)	0.88	1.70	8	1.019	1.56		this work
$(Ph_2MeSiC_5H_4)_2Yb(\mu\text{-Cl})_2Li(Et_2O)_2$	μ	2.593 (1)	0.858	1.74	8	0.985	1.61	88	21
$(C_5Me_5)_2Yb(\mu\text{-Cl})_2Li(Et_2O)_2$	μ	2.596 (1)	0.858	1.74	8	0.985	1.61	89.3	21
		2.594 (1)	0.858	1.74	8	0.985	1.61		
$Cp^L{}_2Nd(\mu\text{-Cl})_2Li(THF)_2$ [c]	μ	2.774 (2)	0.995	1.75	8	1.109	1.64	97	26
$(C_5Me_5)_2\mathit{Y}\cdot(\mu\text{-}\mathit{Cl})YCl(C_5Me_5)$	μ	2.640 (5)	0.88	1.76	7	1.019	1.62	163	this work
$[(CH_3C_5H_4)_2Yb(\mu\text{-Cl})]_2$	μ	2.628 (2)	0.858	1.78	8	0.985	1.66	98	11
		2.647 (2)	0.858	1.79	8	0.985	1.66		
$[Cp^L{}_2Yb(\mu\text{-Cl})]_2$ [c]	μ	2.65 (1)	0.858	1.79	8	0.985	1.66	100	26
$[Cp^L{}_2Pr(\mu\text{-Cl})]_2$ [c]	μ	2.806 (3)	1.013	1.80	8	1.126	1.68	102	26
		2.816 (3)	1.013	1.80	8	1.126	1.69		
$[(C_8H_8)Ce(THF)_2(\mu\text{-Cl})]_2$	μ	2.855 (2)	1.034	1.82	8	1.143	1.71	106.6	28
		2.935 (2)	1.034	1.90	8	1.143	1.79		
$(C_5Me_5)_2Yb(\mu\text{-Cl})_2AlCl_2$	μ	2.760 (1)	0.858	1.89	8	0.985	1.78	94	21
		2.752 (1)	0.858	1.89	8	0.985	1.77	95	
$(C_5Me_5)_2Y(\mu\text{-}\mathit{Cl})YCl(C_5Me_5)_2$	μ	2.776 (5)	0.88	1.90	8	1.019	1.76	163	this work

[a] Reference 29. [b] Reference 30. [c] $Cp^L = 1,3\text{-}[(CH_3)_3Si]_2C_5H_3$.

point earlier in the series, symmetric $[(C_5Me_5)_2Ln(\mu\text{-}X)]_2$ structures should be stable. On the basis of the structure of $[(C_5Me_5)_2SmH]_2$,[2] samarium may be a large enough metal and the hydride may be a small enough ligand for this to occur.

NMR Studies. The ^1H NMR spectrum of II exhibits a single sharp resonance at δ 2.01 in C_6D_6 at room temperature. Addition of a stoichiometric amount of THF to this sample reproduces the spectrum of $(C_5Me_5)_2YCl(THF)$.[14] In $C_6D_5CD_3$ at room temperature, II displays a single sharp resonance at δ 2.21. As the temperature is lowered, this resonance broadens and eventually at temperatures in the 203–218 K range (depending on concentration) a 1:1:2 pattern is observed. These three resonances are consistent with the asymmetrical solid-state structure for II assuming there is rotation of the C_5Me_5 rings to equilibrate the magnetic environment of all the protons of a given ring. The C_5Me_5 rings on Y(1) are equivalent since they are above and below a pseudomirror plane containing Y(1), Y(2), and the two chloride atoms. The C_5Me_5 rings on Y(2) are not equivalent, however, since one is closer to the bridge chloride and the other is closer to the terminal chloride on the other yttrium atom.

Conclusion

This structural study establishes the fact that asymmetric monohalide-bridged dimeric structures are accessible in organoyttrium (and presumably organolanthanide[7]) systems when the relative sizes of the ligands and the metals are such that symmetrical, doubly bridged structures are sterically prohibited. The ability to manipulate bridging vs. terminal ligation for halide (and hydride and alkyl) substituents is of general importance since terminal ligands often exhibit enhanced reactivity compared to bridging ligands in complexes of this type.[32,33] Structure and consequently reactivity can be varied for a system of general formula $(C_5R_5)_2LnX$ depending on how the following three variables are combined: (a) the R substitution on the ring, (b) the size of the metal, and (c) the size and nature of the X group. For example, for a given choice of R and X, by varying the size of the lanthanide metal, a $[(C_5R_5)_2Ln(\mu\text{-}X)]_2$ system can be changed from sterically unsaturated to sterically saturated to sterically oversaturated[32] with accompanying changes in structure and reactivity. Since the lanthanide elements comprise the largest series of metals in the periodic system with similar chemistry but a gradually changing radial size, they offer unique opportunities for size-based control of structure and reactivity.[34] As more structures of sterically oversaturated complexes such as II are obtained and as further reactivity studies are reported, the details necessary for full exploitation of these principles should become clear.

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Registry No. I, 93895-59-1; II, 94348-89-7; $(C_5Me_5)_2YCl(THF)$, 94348-90-0; $(C_5Me_5)_2YCl_2K(THF)$, 94348-91-1; KC_5Me_5, 94348-92-2; YCl_3, 10361-92-9; LiC_5Me_5, 51905-34-1.

Supplementary Material Available: Tables of thermal parameters and structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

Photochemical Reaction of μ-Ethenylidene Complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ with Acetylenes

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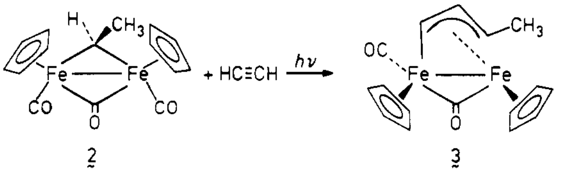
Photolysis of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ and diphenylacetylene led to the formation of metallacyclopentenone $[(C_5H_5)(CO)Fe]_2(\mu\text{-}\eta^2,\eta^2\text{-}COC(C_6H_5)C(C_6H_5)C{=}CH_2)$, **5a**, in 43% yield. Photolysis of **5a** led to loss of CO and rearrangement to give the σ,π-allyl complex $(C_5H_5)(CO)FeFe(C_5H_5)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_5)C(C_6H_5)C{=}CH_2)$, **6**, in 49% yield. The structure of **5a** was determined by X-ray crystallography: monoclinic space group $C2/c$, with unit cell constants a = 26.183 (6) Å, b = 11.163 (2) Å, c = 22.931 (3) Å, β = 106.90 (1)°, and Z = 8.

The interest in the synthesis and reactivity of carbon-bridged bimetallic complexes has intensified in the last few years.[1-4] The study of bridging methylene and related complexes has been the result of their proposed involvement in carbon monoxide reduction chemistry (Fischer–Tropsch synthesis),[5] olefin metathesis,[6] alkyne polymerization,[6-9] and methylene transfer reactions.[10]

Both monometallic carbene complexes and bimetallic bridging carbene complexes have been proposed as intermediates in the metal-catalyzed polymerization of acetylenes.[6] The possible intermediacy of metal carbene complexes in alkyne polymerization prompted Katz[11] to use isolated metal carbene complexes as initiators. He found that metal carbene complexes $(CO)_5W{=}C(C_6H_5)_2$ and $(CO)_5W{=}C(C_6H_5)(OCH_3)$ initiated polymerization of several alkynes.

The reaction of alkynes with bimetallic bridging carbene complexes has recently been explored by several groups. Rudler[7] has found that μ-alkylidene complex $[(CO)_5W\text{-}W(CO)_4](\mu\text{-}\eta^1,\eta^3\text{-}CHCH{=}C(CH_3)_2)$, **1**, initiates the polymerization of 2-butyne. In addition, he was able to isolate the product of the insertion of 2-butyne into the μ-alkylidene bridge of **1**.

Knox[8,12] has studied the photochemical reaction of μ-alkylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$, **2**, with acetylene which gave $(C_5H_5)(CO)FeFe(C_5H_5)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCHCHCH_3)$, **3**. The analogous diruthenium complex $(C_5H_5)(CO)RuRu(C_5H_5)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCHCHCH_3)$ was prepared in a similar manner.



Here we report the photochemical reaction of the bridging ethenylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$,[13,14] **4**, with alkynes. In contrast to the reactivity seen for **2** by Knox,[12] we observed that photolysis of bridging ethenylidene complex **4** with diphenylacetylene and 2-butyne gave metallacyclopentenone complexes **5a** and **5b**, respectively. The X-ray crystal structure of **5a** is reported as well as the further photochemical rearrangement of **5a** to $[(C_5H_5)(CO)FeFe(C_5H_5)](\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_5)C(C_6H_5)C{=}CH_2)$, **6**.

Results

Synthesis of Metallacyclopentenone 5a. Photolysis of a toluene solution of a 1.0:1.7 mixture of *cis*- and *trans*-$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$,[13,14] **4**, and diphenylacetylene under a nitrogen atmosphere for 1.75 h with a Hanovia medium-pressure lamp led to the formation of dark green crystalline metallacyclopentenone $[(C_5H_5)(CO)Fe]_2(\mu\text{-}\eta^2,\eta^2\text{-}COC(C_6H_5)C(C_6H_5)C{=}CH_2)$, **5a**, in 26% yield. Under these conditions, small amounts of starting material were recovered and about 16% of decarbonylated rearrangement product **6** was obtained. In a parallel experiment, the photolysis was run for 1.75 h while CO was bubbled through the solution. Under CO, the metallacyclopentenone **5a** was formed in higher yield (36%), starting material **4** was recovered in 44% yield and

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[†] NSF Postdoctoral Fellow, 1981–1982.

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