

Unusual Eight-membered Rings with Linear Symmetric Methyl Groups from Yttrium and Lutetium Methyl Complexes*

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Abstract

New examples of symmetric linear bridge bonding of methyl groups between two metal ions is demonstrated in the complexes $[M(Cp^*)_2-\mu-Me_2-M'Me_2]_2$ (1) ($M =$ yttrium or lutetium; $M' =$ aluminum or gallium; $Cp^* =$ pentamethylcyclopentadienyl) which are formed by reversible dimerisation of $M(Cp^*)_2-\mu-Me_2-M'Me_2$. X-ray crystallography shows the metal atoms in $Y(Cp^*)_2-\mu-Me_2-AlMe_2$ to be arranged in a flat square array with alternating Y and Al atoms at the vertices, and methyl groups along the sides. The linear Y–C–Al bonds so formed subtend a bond angle of $176^\circ(1)$. Equilibrium constants between $+40^\circ C$ and $-40^\circ C$ for dimerisation to 1 of $Y(Cp^*)_2-\mu-Me_2-AlMe_2$, $Y(Cp^*)_2-\mu-Me_2-GaMe_2$ and $Lu(Cp^*)_2-\mu-Me_2-AlMe_2$ in toluene were obtained, giving the thermodynamic parameters $\Delta H_{eq} = -10.4$, -5.6 and $-8.1(\pm 0.2)$ kcal mol $^{-1}$ and $\Delta S_{eq} = -29.9$, -18.0 and $-27.4(\pm 3)$ e.u. respectively. From NMR data, particularly comparison of coupling constants (J_{C-H} values = 118–124 Hz for linear bridge methyl groups in these systems), the products from reaction of $M(Cp^*)_2-\mu-Me-M(Cp^*)_2Me$ ($M =$ yttrium or lutetium) and $[Y(C_5H_5)_2Me]_2$ are also linearly methyl-bridged tetra-metal complexes $[M(Cp^*)_2-Me-Y(C_5H_5)_2-Me]_2$.

Introduction

As observed for other electrophilic metals such as lithium [1–3] and aluminum [4], the lanthanoids also form organometallic complexes which tend to oligomerise through the formation of hyper-coordinate alkyl bridges [5–11]. This tendency is

obviously favored by the presence or potential presence of coordinative unsaturation at the metal center in the monomer. The oligomers may associate and dissociate rapidly (e.g. on the NMR time-scale) or more slowly (e.g. rate-limiting $k < 10^{-2}$ s $^{-1}$, or so). Detection and characterization of equilibria is not always easy but it is often important to the chemistry. The existence of such equilibria can have a marked effect on apparent rates of reactions and product distributions, dependent on the thermodynamics and kinetics of the equilibrium and the reactivity of the monomer or the oligomer (or both) with a given reagent.

During our studies of the reactivities of bis(pentamethylcyclopentadienyl)-lanthanoid alkyls and hydrides, $M(Cp^*)_2-R$ [12–14], we previously identified facile dimerisation equilibria forming the asymmetric species $[M(Cp^*)_2-R]_2$ (e.g. $M = Lu, Y$; $R = Me, H$) with one bridging and one terminal ligand R. Here we present an interesting further general example of aggregation by alkyl bridging, namely a slow reversible dimerisation of complexes $M(Cp^*)_2-M'Me_4$ ($M = Lu, Y$ and $M' = Al, Ga$) which contain bent penta-coordinate methyl carbon atoms, to give $[M(Cp^*)_2M'Me_4]_2$ containing linear penta-coordinate bridge carbon atoms. NMR data (1H and ^{13}C chemical shifts and C–H coupling constants) given here for this related series of complexes containing methyl ligands in a variety of coordination modes (terminal, bent bridge, asymmetric linear bridge, symmetric linear bridge) show that it is possible to predict the coordination mode of the methyl groups from spectral parameters.

Experimental

All manipulations were routinely carried out in a Vacuum Atmospheres dry box under a slow nitrogen purge, or on a high vacuum line. Solvents were dried thoroughly and distilled under nitrogen prior to use (typically from Na with benzophenone). 1H NMR

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TABLE I. ^1H NMR Data for Yttrium and Lutetium Methyl Aluminates and Methyl Gallates^a

Compound	T ($^{\circ}\text{C}$)	Cp^*	$\text{Me}(\text{bridge})^{\text{b}}$	$J_{\text{Y-H}}^{\text{c}}$	$\text{Me}(\text{terminal})^{\text{d}}$
$\text{LuCp}^*_2\text{Me}_2\text{AlMe}_2$	-40	1.809 (30H)	-0.312 (6H)		-0.262 (6H)
$[\text{LuCp}^*_2\text{Me}_2\text{AlMe}_2]_2$	-40	1.905 (60H)	-0.856 (12H)		-0.042 (12H)
$\text{YCp}^*_2\text{Me}_2\text{AlMe}_2$	-40	1.803 (30H)	-0.506 (6H)	4.7	-0.218 (6H)
$[\text{YCp}^*_2\text{Me}_2\text{AlMe}_2]_2$	-40	1.881 (60H)	-0.982 (12H)	3.2	-0.038 (12H)
$\text{LuCp}^*_2\text{Me}_2\text{GaMe}_2$	-40	1.822 (30H)	-0.293 (6H)		-0.048 (6H)
$[\text{LuCp}^*_2\text{Me}_2\text{GaMe}_2]_2$	-40	1.912 (60H)	-0.739 (12H)		+0.255 (12H)
$\text{YCp}^*_2\text{Me}_2\text{GaMe}_2$	22	1.824 (30H)	-0.495 (6H)	5.0	-0.085 (6H)
	-40	1.812 (30H)	-0.460 (6H)	4.8	+0.076 (6H)
$[\text{YCp}^*_2\text{Me}_2\text{GaMe}_2]_2$	-40	1.889 (60H)	-0.847 (12H)	3.6	+0.267 (12H)
$\text{LuCp}^*_2[\text{Me}_2\text{AlMe}_2]_2\text{YCp}^*_2$	-40	1.913 _{Lu} (30H) 1.875 _Y (30H)	-0.840 (6H) -0.997 (6H)		-0.040 (12H)
$[\text{YCp}^*_2]_2[\text{AlMe}_4][\text{GaMe}_4]$	-40	1.885 (60H)	-0.858 _{Ga} (6H) -0.975 _{Al} (6H)	4.3 3.2	+0.267 (6H) -0.038 (6H)
$[\text{YCp}^*_2\text{MeY}(\text{C}_5\text{H}_5)_2\text{Me}]_2^{\text{e}}$	-80	2.06, 6.22 ^f	-1.689		
$[\text{LuCp}^*_2\text{MeY}(\text{C}_5\text{H}_5)_2\text{Me}]_2^{\text{e}}$	-80	2.07, 6.26 ^f	-1.677		

^a360 MHz spectra in toluene- d_8 (CD_2H solvent peak at 2.089 ppm used as reference). ^bMethyls bridging between Lu, Y and Al, Ga. ^cIn Hz \pm 0.4 Hz. ^dTerminal methyls on Al or Ga. ^eIn methylcyclohexane- d_{14} . ^f Cp^* , C_5H_5 peaks in ratio 3:1.

measurements were made on a Nicolet (G.E.) 361 MHz spectrometer with variable temperature capability. ^{13}C NMR measurements were made on a Bruker WM400. All NMR samples were sealed in 5 mm tubes under nitrogen.

Syntheses of $[\text{M}(\text{Cp}^*)_2\text{Me}]_2$ and $\text{M}(\text{Cp}^*)_2\text{AlMe}_4$ ($\text{M} = \text{Y, Lu}$)^{*} were made according to the procedures referenced in the text [12, 13]. $\text{M}(\text{Cp}^*)_2\text{GaMe}_4$ ($\text{M} = \text{Y, Lu}$) were prepared in an entirely analogous fashion to $\text{M}(\text{Cp}^*)_2\text{AlMe}_4$ and satisfactory elemental analyses were obtained for the pure, white microcrystalline materials. Elemental analysis was performed by Pascher Mikroanalytisches Laboratorium, Bonn, F.R.G.

Results and Discussion

Synthesis and Equilibrium Measurements

The complexes $\text{M}(\text{Cp}^*)_2\text{M}'\text{Me}_4$ ($\text{M} = \text{Lu, Y}$ and $\text{M}' = \text{Al, Ga}$) were prepared as previously reported for $\text{M} = \text{Lu, Yb}$ and Y , $\text{M}' = \text{Al}$ [12, 13], by mixing solvent-free $\text{M}(\text{Cp}^*)_2\text{Me}_2\text{Li}$ with $\text{M}'\text{Me}_3$ ($\text{M}' = \text{Al, Ga}$) in toluene followed by removal of the insoluble LiAlMe_4 by filtration. Concentration of solution with cooling to -30 $^{\circ}\text{C}$ gave the products $\text{M}(\text{Cp}^*)_2\text{M}'\text{Me}_4$ as white microcrystalline solids. Proton NMR spectra for all species are given in Table I, and Fig. 1 shows the actual proton spectrum for $\text{Y}(\text{Cp}^*)_2\text{AlMe}_4$.

NMR spectra of each of these isolated, analytically pure materials show the presence of two complexes in solution, the relative amounts varying with concentra-

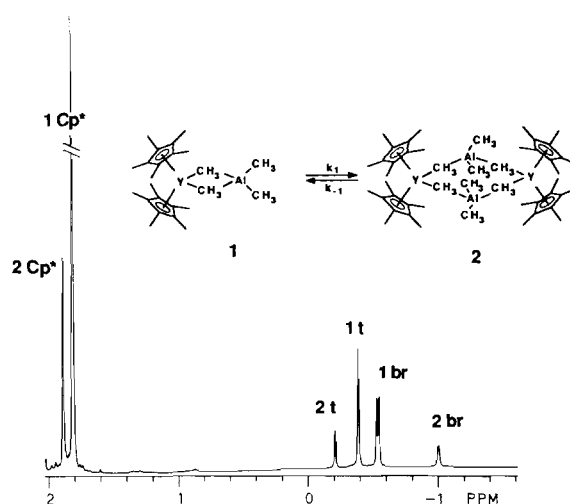


Fig. 1. 360 MHz ^1H NMR spectrum of $\text{Y}(\text{Cp}^*)_2\text{-Me}_2\text{-AlMe}_2$ (1) in toluene- d_8 at 20 $^{\circ}\text{C}$, showing the presence of dimer $[\text{Y}(\text{Cp}^*)_2\text{-Me}_2\text{-AlMe}_2]_2$ (2). Peak assignments are labelled for $\text{C}_5(\text{CH}_3)_5(\text{Cp}^*)$, bridge methyls $\text{Y-CH}_3\text{-Al}(\text{br})$ and terminal methyls $\text{Al-CH}_3(\text{t})$.

tion and temperature. Log-log plots (e.g. Fig. 2) of the concentrations of these two complexes in samples of differing total concentration give slopes of 2 ± 0.2 , at a variety of temperatures between -40 $^{\circ}\text{C}$ and $+40$ $^{\circ}\text{C}$ in toluene- d_8 . These results prove the equilibrium processes under observation to be the dimerisation shown in eqn. (1). Since the NMR peaks are quite sharp and separate, the equilibrium is obviously not rapid on the NMR time-scale, unlike the coordinately unsaturated complexes $\text{M}(\text{Cp}^*)_2\text{Me}$ ($\text{M} = \text{Y, Lu}$) [12-14] which reversibly dimerise giving time-averaged NMR spectra down to -70 $^{\circ}\text{C}$.

We are aware that J. H. Teuben and K. H. den Haan have also recently prepared $\text{Y}(\text{Cp}^)_2\text{AlMe}_4$ and observed dimerisation of the complex.

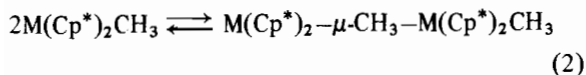


Table I also lists the proton NMR spectra of two 'cross-product' dimers, formed *in situ*. Mixing $\text{Y}(\text{Cp}^*)_2\text{AlMe}_4$ and $\text{Y}(\text{Cp}^*)_2\text{GaMe}_4$ together in toluene- d_8 gives, in addition to the expected two symmetrical dimers, a third dimer with NMR spectrum fully consistent with the formulation $[\text{Y}(\text{Cp}^*)_2\text{AlMe}_4][\text{Y}(\text{Cp}^*)_2\text{GaMe}_4]$, with $\text{Al}(-\text{C}-\text{Y}-\text{C}-)_2$ ring structure. Variation of the relative amounts of the two reactants gave the three dimers in proportions consistent with random distribution of the monomers, *i.e.* there is no special energetic advantage to formation of the asymmetric dimer. The same observation holds true for formation of $[\text{Y}(\text{Cp}^*)_2\text{AlMe}_4][\text{Lu}(\text{Cp}^*)_2\text{AlMe}_4]$, with $\text{Y}(-\text{C}-\text{Al}-\text{C}-)_2$ ring structure, from $\text{Y}(\text{Cp}^*)_2\text{AlMe}_4$ and $\text{Lu}(\text{Cp}^*)_2\text{AlMe}_4$.

Crystal Structure of $[\text{Y}(\text{Cp}^*)_2\text{AlMe}_4]_2$

Crystals of $[\text{Y}(\text{Cp}^*)_2\text{AlMe}_4]_2$ were grown by slow cooling from a toluene solution. The crystals are extremely air-sensitive and produced broad and often multiple diffraction spots. At room temperature, the best crystal (so far) was found to be monoclinic, space group $P2_1/n$, with unit cell parameters of: $a = 12.169(3)$; $b = 12.519(2)$, $c = 16.799(2)$ Å, $\beta = 99.97(2)^\circ$, $V = 2521(2)$ Å³. A data set was collected on this crystal, but only 1679 out of 6407 reflections measured were found with $F2 > 3s(F2)$. In an attempt to improve the quality of the data, the temperature of the crystal was reduced to -70°C (it had been previously determined that the crystals underwent a phase change when cooled to -100°C). Half-way through the data collection at -70°C , the crystal changed phase and destroyed its 'single-crystal' character.

The structure was then solved and refined using the room temperature data. The initial isotropic refinement of all the non-hydrogen atoms clearly showed that many of the atoms associated with the C_5Me_5 rings had high thermal parameters. Attempts to refine these atoms with anisotropic parameters yielded several 'non-positive definite' ellipsoids. ORTEP drawings of those atoms which did refine showed high in-plane motions. In the final cycles, only the yttrium was refined with anisotropic parameters. The refinement converged at $R = 0.110$ and $R_w = 0.129$ and the resulting ORTEP is shown in Fig. 3. Further work on this structure has been suspended in the hopes of obtaining better crystals from other solvents or better crystals of related complexes.

The poor scattering from these crystals is obviously the result of the large thermal motions of the C_5Me_5 rings. While caution must be seriously exercised in reviewing the results, it is clear that the

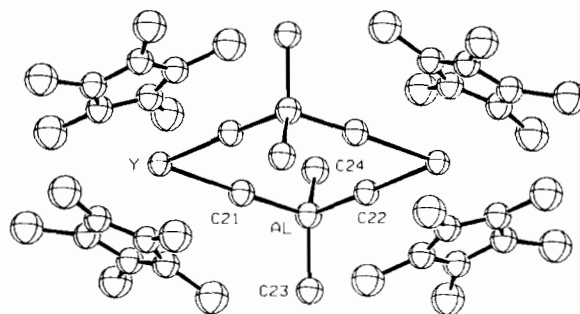


Fig. 3. Molecular structure of $[\text{Y}(\text{Cp}^*)_2\text{AlMe}_4]_2$ whose center corresponds with a crystallographic center of inversion. The atoms were drawn with arbitrary radii.

complex is dimeric with a planar, square-shaped $\text{Y}(\text{C}-\text{Al}-\text{C})_2\text{Y}$ ring in which the $\text{Y}-\text{C}-\text{Al}$ angles are essentially linear. Some of the more notable bond parameters are: bond lengths $\text{Y}-\text{C}(21)$, 2.65(2); $\text{Y}-\text{C}(22)'$, 2.67(2); $\text{Al}-\text{C}(21)$, 2.07(3); $\text{Al}-\text{C}(22)$, 2.07(2); $\text{Al}-\text{C}(23)$, 1.98(3); $\text{Al}-\text{C}(24)$, 2.02(2) Å; and angles $\text{C}(21)-\text{Y}-\text{C}(22)'$, $84.9(7)$; $\text{C}(21)-\text{Al}-\text{C}(22)$, $101.5(9)$; $\text{Y}-\text{C}(21)-\text{Al}$, $177(1)$; $\text{Y}-\text{C}(22)'\text{-Al}'$, $176(1)^\circ$.

Generality of Linear Bridges in Lanthanoid Alkyls

Given these observations concerning the ease of formation of hypervalent alkyls in these lanthanoid systems even to the point of forming eight-membered rings with four bridging methyl groups, and the potential importance of such equilibria in the interpretation of mechanistic studies, we chose a further example to test the generality of multiple aggregation.

The monomers $\text{M}(\text{Cp}^*)_2\text{Me}$ ($\text{M} = \text{Y}, \text{Lu}$) reversibly dimerise to the asymmetric linear-bridged dimer shown in eqn. (2), which has a single $\text{M}-\text{CH}_3-\text{M}$ bond, because the pentamethylcyclopentadienyl ligands are sufficiently bulky to disallow formation of two bent bridge-methyl bonds. (Such bonding would cause a shortening of the metal-metal axis with unfavorable steric consequences. Undoubtedly the symmetric structure could form with larger metal ions.) Less hindered $[\text{M}(\text{C}_5\text{H}_5)_2\text{Me}]_2$ is a symmetric doubly bent bridged dimer. Upon mixing equal amounts of $[\text{Y}(\text{Cp}^*)_2\text{Me}]_2$ with $[\text{Y}(\text{C}_5\text{H}_5)_2\text{Me}]_2$ in toluene or hexane, a new single sharp high-field $\text{Y}-\text{CH}_3$ resonance is observed at 20°C in the NMR spectrum, assigned to the product 3 in Fig. 4. Upon cooling to -90°C only a single species is still seen. Excess of either of the reagents in the solution gives a separate high-field resonance showing that exchange of methyl groups between 3 and the reagent dimers is slow on the NMR time-scale. However use of $\text{Y}(\text{Cp}^*)_2-^{13}\text{CH}_3$ gives complete scrambling of the label into excess $[\text{Y}(\text{C}_5\text{H}_5)_2\text{Me}]_2$ virtually upon mixing, showing that chemically such methyl exchange is fast. Chemical shifts and coupling constants

(see Tables I and III) support the structure of the product as the eight-membered ring **3**. In particular, the value of $J_{C-H} = 123.9$ Hz is sufficiently large so as to preclude assignment of the product as the dimer $[Y(C_5H_5)_2Me_2YCp^*_2]$ with two bent bridge-methyls.

A completely analogous reaction occurs between $[LuCp^*_2Me]_2$ and $[Y(C_5H_5)_2Me]_2$ giving $[LuCp^*_2MeY(C_5H_5)_2Me]_2$ with NMR spectra qualitatively identical to those for **3** (see Tables I and III), except that the bridge carbons are split into a doublet by Y (as expected) rather than the triplet observed for **3** ($Y^{89}I = 1/2$).

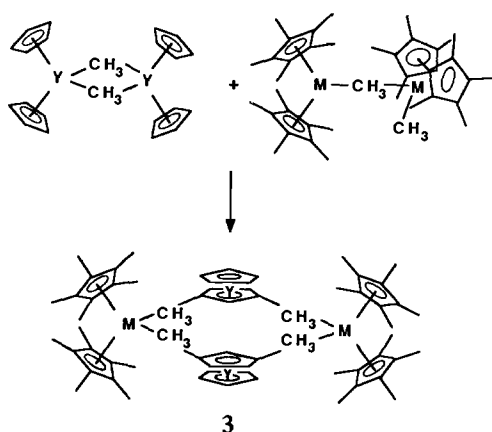


Fig. 4. Formation of an eight-membered $(Y-CH_3)_4$ organometallic ring from two $(Y-CH_3)_2$ dimers.

Methyl Type from Spectral Data

Coupling constants for a representative group of organolanthanoids are shown in Table III. These data strongly suggest that one can use a combination of J_{C-H} and J_{C-Y} to differentiate the various coordination geometries of methyl groups shown in Fig. 5. Indeed, spectroscopic evidence is particularly useful

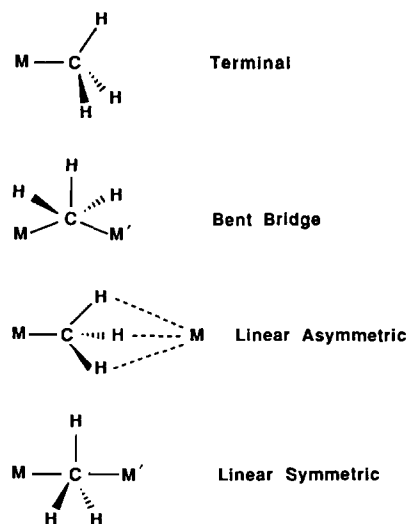


Fig. 5. Four observed bonding modes for methyl groups in lanthanoid organometallic complexes.

TABLE III. Coupling Constants of Yttrium and Lutetium Complexes^a

	T (°C)	Me(ring) C-H	Me(bridge) C-H	Y-C	Me(terminal) C-H	Methyl type
$LuCp^*_2Me \cdot THF$ ^b	20	124.7			108.3	terminal
$YCp^*_2Me \cdot THF$ ^b	20	124.7		56.9, d	108.0	terminal
$LuCp^*_2Me \cdot ether$ ^b	20	125.0			108.9	terminal
$YCp^*_2Me \cdot ether$ ^b	20	124.9		56.0, d	108.7	terminal
$[Y(C_5H_5)_2Me]_2$	-60		104.3	25.2, t		bent bridge
$LuCp^*_2Me_2AlMe_2$	-60	125.8	108.4		[111.3]	bent bridge
$YCp^*_2Me_2AlMe_2$	0	125.4	107.8	12.6, d	[111.0]	bent bridge
$LuCp^*_2Me_2GaMe_2$	-60	125.8	113.5		[118.7]	bent bridge
$YCp^*_2Me_2GaMe_2$	-40	125.8	113.9	11.3, d	[118.2]	bent bridge
$[LuCp^*_2Me]_2$	-80	(125.3, 124.6)	117.5			linear asym.
					107.9	terminal
$[YCp^*_2Me]_2$	-80	125av	119.8	42.7, d		linear asym.
				51.1, s	107.4	terminal
$[LuCp^*_2Me_2AlMe_2]_2$	-60	125.0	117.5		[111.3]	linear sym.
$[YCp^*_2Me_2AlMe_2]_2$	0	125.9	118.0	n.o. ^c	[109.6]	linear sym.
$[LuCp^*_2Me_2GaMe_2]_2$	-60	125.2	123.2		[117.2]	linear sym.
$[YCp^*_2Me_2GaMe_2]_2$	-40	125.8	122.0	n.o. ^c	[117.5]	linear sym.
$[YCp^*_2MeY(C_5H_5)_2Me]_2$ (3)	-80	124.4	123.9	13.3, t		linear sym.
$[LuCp^*_2MeY(C_5H_5)_2Me]_2$	-80	125.0	123.8	11.2, d		linear sym.

^aCoupling constants in Hz. Values in brackets are for methyl groups attached to Al or Ga.

^bSee ref. 12 and 17.

^cNot observed.

in systems where such facile (and in some cases multiple) equilibria exist in solution.

The term 'linear asymmetric' is used to denote a geometry having a linear (or close to linear) arrangement of $M-CH_3-M'$, but where the methyl group retains a distorted tetrahedral geometry. In this case $M-CH_3$ acts as a Lewis base, probably through the hydrogen atoms or C-H bonds, and M' is the Lewis acid. Inversion of the methyl group is energetically disfavored based on formal charge considerations. Such bonding was established crystallographically many years ago in $[InMe_3]_4$ [18]. Where symmetry in the molecule permits fast cooperative inversion of linear bridging methyl groups, or even a static, flattened CH_3 with more delocalized $M-C-M'$ bonding, the geometry is called 'linear symmetric'. Stucky's structure of $[LiBMe_4]_4$ [3], Grubb's complex containing a $Zr-Me-Zr$ unit [19], and Schleyer's crystallographically characterized tetramer [sodium benzyl] $_4$ [20] are pertinent examples, but this bonding type remains unusual. Geometries of one or more of the complexes listed for each methyl type in Table III have been established by X-ray crystallography, e.g. $MCp^*_2Me \cdot L$ ($M = Y, Lu$; $L = THF, ether$) [17], $[LuCp^*_2Me]_2$ [17, 21] and $YCp^*_2Me_2AlMe_2]_2$. Trends in magnitude of J_{C-H} from Table III are: bent bridge (104–114 Hz) < terminal (107–109 Hz) < linear asymmetric (117–119 Hz) < linear symmetric (120–124 Hz). Clear differentiation between the latter two geometries is possible for $Y-CH_3-Y$ since the former (asymmetric) methyl carbon shows coupling to only one Y atom (as for the bridge-methyl in $[YCp^*_2Me]_2$), whereas the latter (symmetric) methyl shows equivalent coupling to both Y atoms, as in 3. J_{Y-C} for the linear asymmetric methyl is also closer to the value for a terminal methyl group than bent or linear symmetric bridge bonds, presumably because the methyl group is less distorted from tetrahedral and the Y(sp²-coupled)-C distance less elongated.

Another useful spectroscopic trend is that linear (both symmetric and asymmetric) bridge bonds occur at higher field than terminal or bent bonds in the

same or closely analogous complex (by about 0.5 ppm in the proton spectrum and 3–13 ppm in the carbon spectrum), and linear symmetric are to higher field than linear asymmetric.

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