

RECENT TRENDS IN DIVALENT ORGANOLANTHANIDE CHEMISTRY

S JAGANNATHA SWAMY

*Department of Chemistry, University College, Kakatiya University,
Warangal-506 009, AP, India*

(Received 6 June 1988; Accepted 14 October 1988)

The interaction of small molecule substrates with highly ionic trivalent organolanthanide complexes was found to be less probable and not potential for its exploitation as in the case of organometallic chemistry of transition metals. The recent reports indicate that the divalent organolanthanides [Yb(II) and Sm(II)] react with neutral molecules resulting in very interesting compounds having useful reaction chemistry. This is further facilitated by the investigation of different synthetic routes to prepare the divalent organometallics having useful reaction sites for further modification of the environment around divalent lanthanide metal ion.

The synthesis of the first Yb(II) compound containing an active site and a cyclopentadienide ring and some new soluble Sm(II) compounds is achieved by metathesis reactions and the compounds were characterised by elemental analysis, IR, NMR, Mass spectral studies and X-ray diffraction method.

The synthesis, structures and reactions of some novel, highly reactive divalent organolanthanide compounds is discussed along with some recent developments achieved in the field of divalent organolanthanide chemistry.

Key Words : Divalent Organolanthanide Chemistry, Transition Metals

INTRODUCTION

THE organometallic chemistry of trivalent lanthanides has been extensively studied in detail since 1950s.¹⁻⁵ The last decade has witnessed a bulk of literature on divalent organolanthanides. Although, the compounds of lanthanides in $+2$ state can be generated by irradiation of trivalent ions doped in CaF_2 for almost all lanthanides,⁶ only three elements have divalent states, which are chemically accessible in organometallic systems under normal conditions: Eu, Yb and Sm [$\text{Eu}^{3+}/\text{Eu}^{2+} = -0.35\text{V}$; $\text{Yb}^{3+}/\text{Yb}^{2+} = -1.15\text{V}$; $\text{Sm}^{3+}/\text{Sm}^{2+} = -1.55\text{V}$]. These data indicate that Eu^{2+} is the most stable divalent lanthanide ion, while Sm^{2+} is the most reactive one and the Yb^{2+} is intermediate. Therefore, much attention was paid on the organometallic chemistry of Yb(II) and Sm(II). Initially the organometallic compounds of Yb(II) were prepared in large number and their reactions were thoroughly investigated,⁷⁻¹⁴ mainly because of the solubility of these compounds in different solvents. The insolubility of the first prepared Sm(II) compounds with cyclopentadienyl^{15,16} and methylcyclopentadienyl¹⁷ was responsible for the delay in growth of the organometallic chemistry of this ion.

The preparation of the soluble derivative of Sm(II) using the bulky pentamethylcyclopentadienide^{18,19} is the major breakthrough in the organometallic chemistry of Sm(II). In view of this increasing interest in the chemistry of divalent organolanthanides, we undertook the preparation and characterisation of some novel compounds of Sm(II) and Yb(II). The present paper deals with the synthesis and characterisation of the compounds—(C₅Me₅)₂Sm.DME (I), [C₅H₄(CH₂)₃C₅H₄] Sm(THF)₂ (II), [C₅H₄(CH₂)₃C₅H₄] Sm(THF)₂ (III), C₅H₅YbCl(THF)₂ (IV), C₅H₅YbCl.DME (V), C₅Me₅YbCl(THF)₂ (VI) and C₅Me₅YbCl.DME (VIII), along with few of the recent novel achievements made by some investigators during last few years in this field.

EXPERIMENTAL

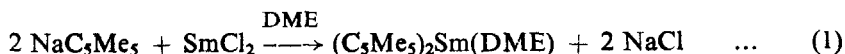
The compounds described here are extremely air and moisture sensitive. Therefore, both synthesis and subsequent manipulations of these compounds are carried out using Schlenk flasks and Vacuum line in an atmosphere of dried oxygen-free argon. The solvents tetrahydrofuran (THF), dimethoxyethane (DME), benzene and pentane were dried and freed of oxygen by distilling under argon from blue sodium benzophenone ketyl immediately prior to use. d₈-THF and d₆-benzene were dried by refluxing over sodium for several hours and distilling before use. Anhydrous YbCl₃, SmCl₃, YbCl₂, SmCl₂ salts and solutions of NaC₅H₅, NaC₅Me₅ and C₅H₄(CH₂)₃C₅H₄ Na₂ were prepared by the methods reported elsewhere. Elemental analyses were performed on a Perkin-Elmer CHN-Analyser 240C. Metal analyses were carried out by complexometric titration using dithizone. ¹H-NMR spectra were obtained in sealed 5mm tubes on Bruker WP 80 SI and Bruker WH 270 instruments. Infrared spectra were recorded as paraffin mulls between CsI plates using a Perkin-Elmer 560 B (200–4000 cm⁻¹) spectrophotometer. The mass spectra was recorded on a Varian MAT 311 A Spectrometer. The single crystal X-ray diffraction studies were carried out on Enraf-Nonius CAD-4 diffractometer using the program SHELX for all calculations.

The details of the synthesis were presented in our earlier communications.^{20–22}

RESULTS AND DISCUSSION

(i) *Organosamarium(II) Compound in DME*

All of the soluble organometallic compounds of Sm(II) were prepared only in THF.^{18,19} Therefore, only THF coordinated or solvent free compound, (C₅Me₅)₂Sm,²³ are known. To see whether Sm(II) forms any soluble compounds in solvents other than THF, a reaction of SmCl₂ with NaC₅Me₅ was carried out in DME, equation 1, which gave a green soluble Sm(II) compound.



The compound obtained in 70 per cent yield, analysed for 56.05 per cent C, 7.63 per cent H, 28.98 per cent Sm (required 55.97 per cent C, 7.83 per cent H and

29.99 per cent Sm). The $^1\text{H-NMR}$ spectrum of the compound I exhibits ring methyl proton signal at δ 4.18ppm (30 H), while the methylene protons resonance signal of DME at 1.84ppm (4 H). It is interesting to note that the signal of the methyl protons of the coordinated DME are shifted down field (1.9ppm, 6H) compared to that of methylene protons. These two signals are considerably shifted up field side as compared to the uncoordinated DME molecule 3.4ppm (4 H) and 3.2ppm (6 H).

The samarium ion is pseudo-tetrahedrally surrounded by two C_5Me_5 rings and two oxygen atoms of the DME molecule (Fig. 1). The X-ray diffraction studies on a single crystal picked up from the DME solution indicated the presence of a second DME molecule in the crystal lattice. This type of solvation was also reported earlier for a Yb(II) compound.⁸ The uncoordinated DME molecule shows a normal structure, while in the coordinated DME molecule the two oxygen atoms are close to one another (267pm in coordinated DME and 281pm in uncoordinated DME) reflecting the steric crowding of the Sm(II) ion. Table I lists out some of the interesting bonding parameters of analogous Sm(II) and Yb(II) compounds.

The metathetical or disproportionation deed not yield the expected products in the case of divalent organo-lanthanides.⁸ Evans *et al.*,¹⁹ have demonstrated reactions that the reaction between soluble $\text{SmI}_2(\text{THF})_2$ and KC_5Me_5 and that between

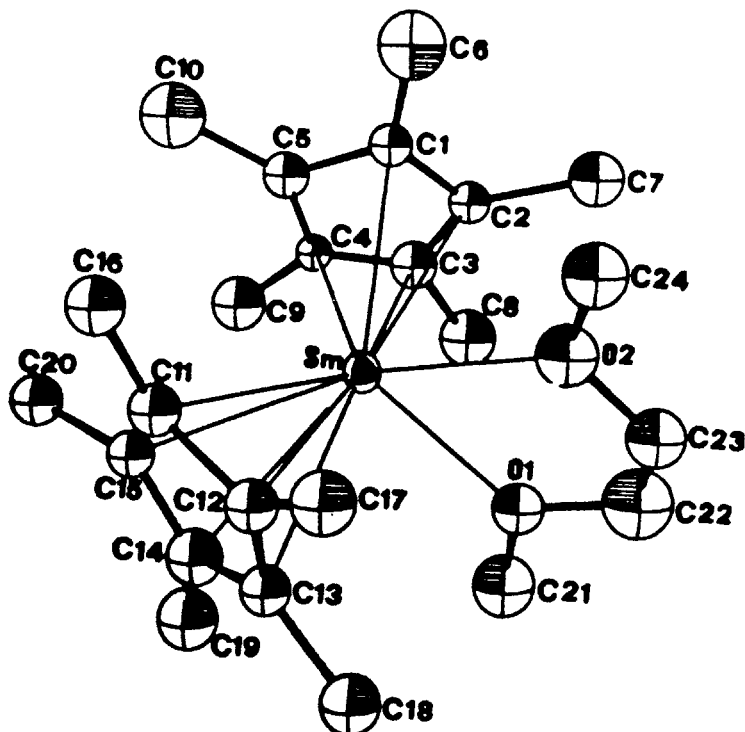


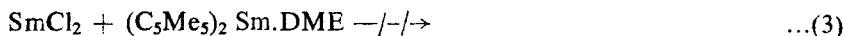
FIG 1 Molecular structure of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{DME})$ showing the atomic numbering

TABLE I
Structural data of $(C_5Me_5)_3Sm(DME)$ and related compounds

Property	$(C_5Me_5)_2Sm^a$	$(C_5Me_5)_2Sm(THF)_2^b$	$(C_5Me_5)_2Sm(DME)^c$	$(C_5Me_5)_2Yb(DME)^d$
Formal Coordination number	6	8	8	8
Average Ln-C distance, pm	279	286	286	272
Range of Ln-C distances pm	277 to 281	281 to 291	279 to 287	260 to 291
Ln — O distance, pm	—	261 & 265	252 & 259	245 & 250
Ring centroid — Ln — ring centroid	140.1°	136.7°	140°	129°
O — Ln — O angle	—	82.6°	62.5°	67.2°

^aRef. 23; ^bRef. 19; ^cOur work; ^dRef. 14

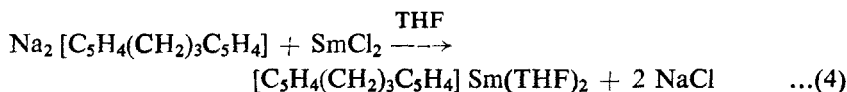
$(C_5Me_5)_2Sm(THF)_2$ and $SmI_2(THF)_2$ in the ratio of 1 : 1 gives the compound containing an active site, $[(C_5Me_5)_2Sm(\mu - I)(THF)_2]_2$. The chloride analogue would be a better compound in the subsequent reactions to get the alkyl derivatives. Our attempts to prepare a chloride analogue using either of the reactions 2 and 3 in DME failed to give the expected product. In reaction 2 only the



bis-(pentamethylcyclopentadienyl) Sm(II) compound was isolated.

(ii) *Divalent Organolanthanides with a Ring Bridged Dicyclopentadienide*

The large bulky organic anions like permethylatedcyclopentadienides were found to offer stability, solubility and crystallinity to many organometallics.²⁴ A ring bridged dicyclopentadienide $[(C_5H_4(CH_2)_3C_5H_4)^{2-}]$ was found to offer stability to the organometallics of the large early lanthanide cations.^{25,26} A reaction was carried out with this reagent to test whether it forms a soluble Sm(II) compound (equation 4).



The reaction has completed in 4 hours to give a purple solution with white precipitate of NaCl. From the solution the compound II was isolated in 80 per cent yield. This is the second soluble Sm(II) compound known to date.

A similar reaction was also carried out using $YbCl_2$ to obtain a Yb(II) analogue, compound III, whose structure was determined by single crystal X-ray

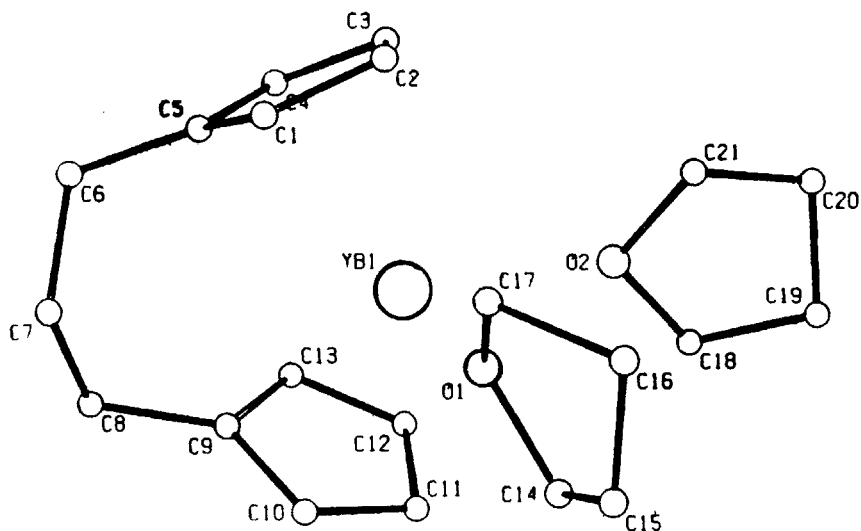


FIG 2 The molecular structure of $[C_5H_4(CH_2)_3C_5H_4] Yb(THF)_2$ with the atomic numbering

TABLE II

Analytical data and properties of $C_5H_4(CH_2)_3C_5H_4 Ln(THF)_2$

Property	Ln = Sm	Ln = Yb
Colour	Purple	Purple
Analysis %	C = 53.98 (54.26) H = 6.45 (6.5) Sm = 31.8 (32.35)	51.1 (51.75) 6.12 (6.2) 34.8 (35.49)
1H NMR ppm	11.6 (8 H) 5.3 & 2.8 (m 6 H) 3.58 (4 α H) 1.73 (4 β H)	5.43, 5.37 (8 H) 2.9 to 2.3 (m 6 H) 3.62 (4 α H) 1.75 (4 β H)
IR spectra, cm^{-1}	3055, 2925, 2870, 1440 1050, 875, 770, 490 365, 250, 220.	3070, 2920, 2875, 1440, 1050, 1015, 862, 775 465, 385, 255, 230.

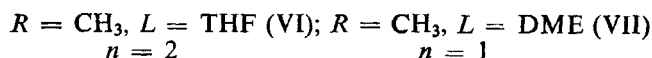
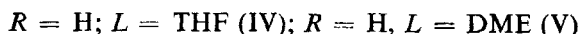
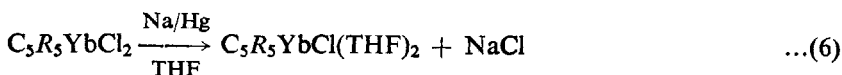
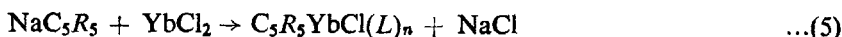
diffraction studies (Fig. 2). The properties of the compounds II and III are presented in Table II.

(iii) Monocyclopentadienyl Ytterbium (II) Compounds with a Reactive Site

Dicyclopentadienyllanthanide(III) chlorides were extensively used as precursors for the preparation of different lanthanide alkyls and hydrides. Such compounds of divalent lanthanides with a reactive site for the modification of the environment around Ln(II) ion, by reaction with metal alkyls or aryls, can be expected to have interesting chemistry. Further, the divalent lanthanide alkyls with a cyclopentadienyl ring may be subjected to hydrogenolysis to get divalent organolanthanide

hydrides, which may possess catalytic properties. The recent reports²⁷⁻³¹ demonstrate the application of the alkyl/aryl lanthanide(II) halides ($RLnX$) in organic synthesis.

Perusal of the literature indicates that only one compound of Sm(II) with a reactive site and cyclopentadienyl ring, $[(C_5Me_5) Sm(\mu - I) (THF)_2]_2$, is reported.¹⁹ Therefore, it is thought worthwhile to prepare the compounds of type $C_5R_5YbCl(L)_n$ using the simple metathetical and reduction reactions (equations 5 and 6).



The properties of these compounds are given in Table III.

TABLE III

Analytical data and properties of compounds $C_5R_5YbCl(L)$

Property	$C_5H_5YbCl(THF)_2$	$C_5H_5YbCl(DME)$	$C_5Me_5YbCl(THF)_2$	$C_5Me_5YbCl(DME)$
Colour	Purple	Green	Purple	Green
Yield %	68	67	75	75
Analysis %	C = 36.91 (37.36) H = 5.12 (5.03) Cl = 8.02 (8.50) Yb = 40.86 (41.44)	28.95 (29.71) 3.92 (4.13)	44.74 (44.31) 6.18 (6.36) 7.58 (7.28)	38.12 (38.75) 5.46 (5.77) — 39.11 (39.91)
¹ H NMR Spectra , ppm	5.60 (5 H) 3.50 (4 α H) 1.63 (4 β H)	6.29 (5 H) 3.11 (4 CH_2) 3.01 (6 CH_3)	1.80 (15 H) 3.58 (4 α H) 1.58 (4 β H)	1.77 (15 H) 1.85 (6 CH_2) 1.68 (4 CH_3)

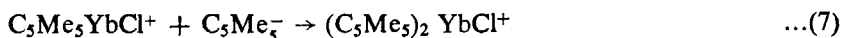
Complete mass spectral investigations of only a very few organolanthanides have been reported.³²⁻³⁴ The mass spectrum of compound VII was recorded and was fully explained (Table IV). In addition to the main peaks presented in the table, peaks of very low intensity were also observed at $m/e = 478$ and 443. The former corresponds to $[(C_5Me_5)_2 YbCl]^+$ and the latter to $[(C_5Me_5)_2 Yb^{III/II}]^+$. Zhou *et al.*³² have also observed ions corresponding to $[(C_5H_5)_3 Nd(Phen) + 1]^+$ and $[(C_5H_5)Nd + 1]^+$ in the mass spectrum of $[(C_5H_5)_2 NdCl(Phen)]$. They have stated that these ions have resulted from tricyclopentadienyl impurities. The ¹H NMR spectra of none of the four compounds, IV to VII, have shown any indication of paramagnetic impurities. Therefore, it is proposed that these

TABLE IV

Mass spectral data of $(C_5Me_5)_2YbCl(DME)$ The relative abundances of the isotopes are given in parentheses

<i>m/e</i>	Ion	I	<i>m/e</i>	Ion	I
41	C_5H_5	1.2	174	Yb(31.84)	0.7
43	C_5H_7	0.8	176	Yb(12.73)	0.2
53	C_5H_6	0.5	205	Yb ¹⁷⁰ Cl ¹³⁵ (2.29)	0.4
55	C_5H_7	0.4	206	Yb ¹⁷¹ Cl ¹³⁵ (10.81)	1.7
65	C_5H_6	0.5	207	Yb ¹⁷² Cl ¹³⁵ (16.48)	2.8
77	C_5H_5	1.1		Yb ¹⁷⁰ Cl ¹³⁷ (0.74)	
79	$C_5H_4CH_3$	1.1	208	Yb ¹⁷² Cl ¹³⁵ (12.18)	2.5
90	DME	0.3		Yb ¹⁷¹ Cl ¹³⁷ (3.5)	
91	C_5H_7	2.2	209	Yb ¹⁷⁴ Cl ¹³⁵ (24.05)	4.8
93	$C_5Me_5-3CH_2$	1.4		Yb ¹⁷² Cl ¹³⁷ (5.34)	
103	$C_5Me_5-2CH_3-H_2$	0.3	210	Yb ¹⁷² Cl ¹³⁷ (3.95)	0.6
105	$C_5Me_5-2CH_3$	3.2	211	Yb ¹⁷² Cl ¹³⁵ (9.62)	2.9
107	$C_5Me_5-2CH_3$	0.9	213	Yb ¹⁷² Cl ¹³⁷ (3.12)	0.5
115	$C_5Me_5-CH_2-3H_2$	1.0	306	$C_5Me_5Yb^{171}$ (12.77)	0.6
117	$C_5Me_5-CH_2-2H_2$	0.4	307	$C_5Me_5Yb^{172}$ (19.47)	0.9
119	$C_5Me_5-CH_2-H_2$	3.6	308	$C_5Me_5Yb^{172}$ (14.39)	0.7
120	$C_5Me_5-CH_2$	1.0	309	$C_5Me_5Yb^{174}$ (28.41)	1.1
121	$C_5Me_5-CH_2$	2.6	311	$C_5Me_5Yb^{174}$ (11.36)	0.4
133	$C_5Me_5-H_2$	0.5	340	$C_5Me_5Yb^{170}Cl^{134}$ (2.04)	1.8
134	C_5Me_5-H	0.9	341	$C_5Me_5Yb^{171}Cl^{134}$ (9.65)	3.4
135	C_5Me_5	2.6	342	$C_5Me_5Yb^{172}Cl^{135}$ (14.71)	3.5
136	$C_5Me_5 + H$	1.8	343	$C_5Me_5Yb^{172}Cl^{135}$ (10.88)	5.8
170	Yb(3.03)	0.1	344	$C_5Me_5Yb^{174}Cl^{135}$ (21.47)	2.2
171	Yb(14.31)	0.3	345	$C_5Me_5Yb^{172}Cl^{137}$ (3.52)	3.6
172	Yb(21.82)	0.4	346	$C_5Me_5Yb^{174}Cl^{135}$ (8.58)	0.9
173	Yb(16.13)	0.3		$C_5Me_5Yb^{174}Cl^{137}$ (6.96)	

ions of *m/e* 478 and 443 have formed under electron impact as show in equation 7.



(iv) Some Recent Novel Investigations of Divalent Organolanthanides

(a) Analogues of Ferrocene—It is generally accepted fact that the divalent lanthanide ions require more number of ligands to form stable compounds. The reported compounds have two bulky pentamethylcyclopentadienyls and one or two coordinated solvent molecules to attain a coordination number of 7 or 8. But the attempts of Evans *et al.*^{23,35} and Andersen *et al.*³⁶ in obtaining base free *bis*-(pentamethylcyclopentadienyl) Ln(II) compounds by careful sublimation of $(C_5Me_5)_2 Ln(THF)_2$ resulted in analogues of ferrocene. The three compounds of Sm(II), Eu(II) and Yb(II) were found to have unique bent structures. Traditionally, the bonding in organolanthanide complexes has been thought to be predominantly ionic due to the limited radial extension of the 4f valence orbitals,³⁷ and also that

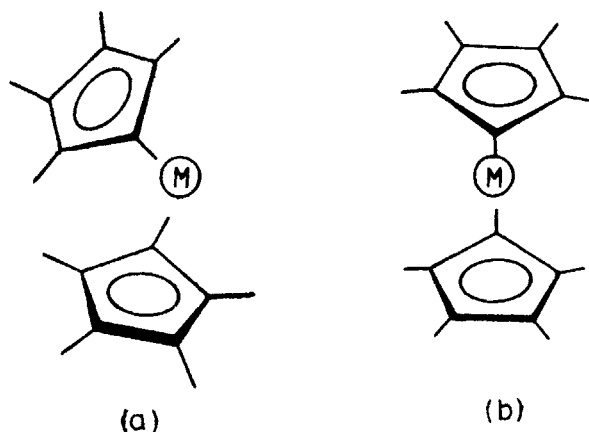


FIG 3 Geometries for bis-(pentamethylcyclopentadienyl) metal complexes : (a) nonparallel rings; (b) parallel rings

the structures are controlled to a large degree by electrostatic factors.³⁸ For the ionic complexes of two $C_5Me_5^-$ anions and Ln(II) cations, simple electrostatic considerations would suggest a structure with parallel C_5Me_5 rings (Fig 3b). Steric factors would also favour a structure with parallel rings (Fig. 3b) rather than a bent metallocene structure with nonparallel rings (Fig. 3a). Any incipient covalent interactions due to the possibility of involvement of 5d or 6s energy levels (which is more favourable for Ln(II) ions than for Ln(III) ions,³⁹ may force the molecule to have bent structure, but existence of such interactions are not known. The molecular orbital studies of these compounds were also reported.^{36,40,41} A parallel ring structure was found to be more stable than a bent structure, although distortions from the parallel ring arrangement were not energetically costly.^{40,41} For a rationalisation of the tilted ring structure, one may have to resort to electrostatic considerations within the polarizable ion model.^{42,43} This model has proven useful for understanding structural trends in metal di- and trihalides and attributes bent structures of metal dihalides to increased attractive interaction between the metal and halide ions of the types—charge-induced dipole, dipole-charge and dipole-dipole. These outweigh the increased interhalogen charge-charge and induced dipole-dipole repulsion. This argument is extended to provide a nice electrostatic rationale for the bent structures of $(C_5Me_5)_2 Ln(II)$ without involving 4f-orbital participation and without involving high energy 5d-and 6s orbitals.

(b) Reactions of $(C_5Me_5)_2Yb$ with $MeC\equiv CMe$ and $(n^2 - C_2H_4) Pt(PPh_3)_2$

Insertion of an olefin into a metal-carbon bond is a fundamental and reasonably well-known process in d-transition metal organometallic chemistry.^{44,45} It is generally assumed that coordination of the olefin to the metal centre is a prerequisite to insertion. In 1986, Andersen *et al.*,⁴⁶ have observed that the $(C_5Me_5)_2Yb$ initiates polymerisation of ethylene. This led to the investigation

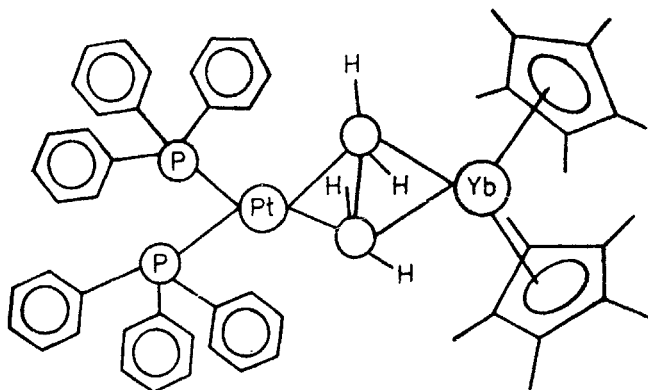


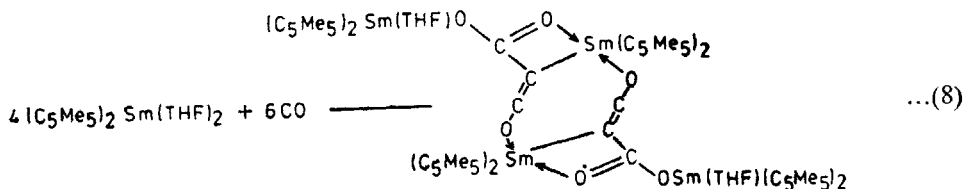
FIG 4 The structure of $(C_5Me_5)_2Yb(\mu-C_2H_4)Pt(PPh_3)_2$

of the possibility of formation of f-transition metal compounds with neutral unsaturated compounds. The interaction of $MeC \equiv CMe$ with $(C_5Me_5)_2Yb$ resulted in diamagnetic $(C_5Me_5)_2Yb(MeC \equiv CMe)$.⁴⁷ The methyl resonance signals of the 2-butyne were effected much on bonding to $Yb(II)$ [shifts from δ 1.52ppm in free 2-butyne to 1.27 on coordination]. A deshielding of methyne and methyl carbons in $^{13}C\{^1H\}$ NMR spectrum was observed (74.6 to 76.9 and 3.08 to 3.76 respectively). The molecular structural studies indicate that the C-C distance between methyne carbons decreases from 1.21 Å to 1.154 Å and the C-C-C(Me) angle decreases to 177.4° from linearity. This shows that a very little or no π -back-bonding is involved in Yb-acetylenic bond.

Similar changes were observed when an ethylenic complex $(n^2 - C_2H_4)Pt(PPh_3)_2$ is coordinated to $(C_5Me_5)_2Yb$ through C_2H_4 moiety⁴⁸ (Fig. 4).

(c) Reduction of CO with $(C_5Me_5)_2Sm(THF)_2$

A unique reduction of CO was noticed in the reaction of $(C_5Me_5)_2Sm(THF)_2$ with CO^{49,50} (equation 8).



The dimeric product contains four Sm(III) centres and the equivalent of six CO molecules, which have been reduced by four electrons, and this reductive homologation formed two ketene-carboxylate units. The most interesting feature in the formation of the ketenecarboxylate complex is that complete cleavage of one CO triple bond has occurred to give the central oxygen-free carbon of the C=C-C skeleton. Although CO cleavage is thought to occur in

were investigated extensively. The characteristic reducing reactions of Sm(II) to form Sm(III) intermediates in almost all of its reactions with neutral molecules show its useful reaction chemistry, while the formation of addition compounds, without oxidation, by Yb(II) derivatives throws light on the structure and bonding in the divalent organolanthanides. It is clear that much can be added to the field of organometallic chemistry by way of diverse investigations on divalent organolanthanide complexes.

ACKNOWLEDGEMENTS

The author would like to thank Professor H Schumann, Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, FRG for providing facilities to carry out the work and to the German Academic Exchange Service (DAAD) for a post-doctoral fellowship. He is also grateful to the authorities of Kakatiya University, Warangal, for sanctioning leave to avail the fellowship.

REFERENCES

- 1 T J Marks *Progr inorg Chem* **24** (1978) 51
- 2 W J Evans In : *The Chemistry of the Metal-Carbon Bond* (Eds : F R Hartley and S Patai) Wiley New York (1982) 489
- 3 H Schumann *Angew Chem int Edn* **23** (1984) 474
- 4 H Schumann and W Genthe In : *Handbook on the Physics and Chemistry of Rare Earths* (Eds K A Gschneider and L Eyring) Amsterdam Vol 7 (1984) pp 445
- 5 H Schumann In : *Fundamental and Technological Aspects of Organof-Element Chemistry* (Eds T J Marks and I L Fragals) D Riedel Dordecht (1985) 1
- 6 N B Mikheev *Inorg Chim Acta* **94** (1984) 241
- 7 F Calderazzo, R Pappalardo and S Losi *J inorg nucl Chem* **28** (1966) 987
- 8 T D Tilley, R A Andersen, B Spencer, H Rueben, A Zalkin and D H Templeton *Inorg Chem* **19** (1980) 2999
- 9 P L Watson *J chem Soc chem Commun* (1980) 652
- 10 M F Lappert, P I W Yarrow, J L Atwood, R Shakir and J Holton *J chem Soc chem Commun* (1980) 987
- 11 H A Zinnen, J J Pluth and W J Evans *J chem Soc chem Commun* (1980) 810
- 12 T D Tilley, R A Andersen, B Spencer and A Zalkin *Inorg Chem* **21** (1982) 2647
- 13 T D Tilley, R A Andersen and A Zalkin *Inorg Chem* **22** (1983) 856
- 14 G B Deacon, P I Mackinon, T W Hambley and J C Taylor *J organometal Chem* **259** (1983) 91
- 15 G W Watt and E W Gillow *J Am chem Soc* **91** (1969) 775
- 16 J L Namy, P Girard, H B Kagan and P E Caro *Nouv J Chim* **5** (1981) 479
- 17 W J Evans and H A Zinnen (*unpublished*)
- 18 W J Evans, I Bloom, W E Hunter and J L Atwood *J Am chem Soc* **103** (1981) 6507
- 19 W J Evans, J W Grate, H W Choi, I Bloom, W E Hunter and J L Atwood *J Am chem Soc* **107** (1985) 941
- 20 S Jagannatha Swamy and H Schumann *J organometal Chem* **334** (1987) 1
- 21 S Jagannatha Swamy, J Loebel, J Pickardt and H Schumann *J organometal Chem* **353** (1988) 27
- 22 S Jagannatha Swamy, J Loebel and H Schumann (*communicated*)
- 23 W J Evans, L A Hughes and T P Hanusa *J Am chem Soc* **106** (1984) 4270
- 24 P T Wokzanski and J E Bercaw *Accts chem Res* **13** (1980) 121, and references quoted therein

- 25 J N John and M Tsutsui *Inorg Chem* **20** (1980) 177
- 26 C Quian, C Ye, H Lu, Y Li and Y Huang *J organometal Chem* **263** (1984) 333 and references quoted therein
- 27 D F Evans, G V Fazakerley and R F Philips *J chem Soc chem Comm* (1970) 244
- 28 P Girard, J L Namy and H B Kagan *J Am chem Soc* **102** (1980) 2693
- 29 H B Kagan and J L Namy *Tetrahedron* **42** (1986) 6573 and references cited therein
- 30 J R Long In : *Handbook on the Physics and Chemistry of Rare Earth* (Eds K A Gschneidner and L Eyring) Elsevier Amsterdam (1986) p 335 and references quoted therein
- 31 K Yokoo, Y Yamanaka, T Fukagawa, H Taniguchi and Y Fujiwara *Chem soc Japan chem Lett* (1983) 1301
- 32 J Zhou, Y Ge and C Qian *Synth React inorg met-org Chem* **14** (1984) 651
- 33 R G Hayes and J L Thomas *Organometal Chem Rev A7* (1971) 1
- 34 C Ni, Z Zhang, D Deng and C Qian *J organometal Chem* **306** (1986) 209
- 35 W J Evans, L A Hughes and T P Hanusa *Organometallics* **5** (1986) 1285
- 36 R A Andersen J M Boncella, C J Burns, R Blom, A Haaland and H V Volden *J organometal Chem* **312** (1986) C49
- 37 A J Freeman and R E Watson *Phys Rev* **127** (1962) 2058
- 38 K N Raymond and C W Eigenbrot Jr *Accts chem Res* **13** (1980) 276
- 39 G H Dieke In : *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Eds H M Crosswhite and H Crosswhite) Wiley New York (1968) p 153
- 40 J V Oritz and R Hoffmann *Inorg Chem* **24** (1985) 2095
- 41 J C Green, D Hohl and N Rösh *Organometallics* **6** (1987) 712
- 42 E S Rittner *J chem Phys* **19** (1951) 1030
- 43 D L Hindenbrand *J electrochem Soc* **126** (1979) 1396
- 44 A Yamamoto *Organotransition Metal Chemistry* Wiley New York (1986) Ch 7
- 45 H Sinn and Kaminsky *Adv organometal Chem* **18** (1980) 99
- 46 R A Andersen, J M Boncella, C J Burns, J C Green, D Hohl and N Rösh *J chem Soc chem Commun* (1986) 405 (*unpublished results*)
- 47 C J Burns and R A Andersen *J Am chem Soc* **109** (1987) 941
- 48 C J Burns and R A Andersen *J Am chem Soc* **109** (1987) 915
- 49 W J Evans, J W Grate, L A Hughes, H Zhang and J L Atwood *J Am chem Soc* **103** (1981) 6507
- 50 W J Evans, J W Grate, L A Hughes, H Zhang and J L Atwood *J Am chem Soc* **107** (1985) 3728
- 51 H H Storch, N Golumbic and R B Anderson *The Fisher-Tropsch Reaction and Related Syntheses* Wiley New York (1951)
- 52 W J Evans, I Bloom, W E Hunter and J L Atwood *J Am chem Soc* **105** (1983) 1401
- 53 W J Evans and D K Drummond *J Am chem Soc* **108** (1986) 7440 and references cited therein
- 54 W J Evans, I Bloom, J W Grate, L A Hughes, W E Hunter and J L Atwood *Inorg Chem* **24** (1985) 4620
- 55 W J Evans and T A Ulibarri *J Am chem Soc* **109** (1987) 4292
- 56 W J Evans, L R Chamberlin and J W Zillev *J Am chem Soc* **109** (1987) 7209