ORGANOMETALLIC COORDINATION COMPLEXES OF THE BIS(PENTAMETHYLCYCLOPENTADIENYL)-ALKALINE EARTH COMPOUNDS, $(Me_5C_5)_2MLn$, WHERE M IS Mg, Ca, Sr, OR Ba AND Me_5C_5BeCl. *

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Summary

The ether complexes, $(Me_5C_5)_2Sr(OEt_2)$ and $(Me_5C_5)_2Ba(thf)_2$, have been isolated from reactions of SrI_2 in Et_2O or BaI_2 in thf with NaC_5Me_5. The base-free compounds were isolated by the "toluene-reflux" method. The coordination compounds $(Me_5C_5)_2M(bipy)$ (M = Mg, Ca, Sr, Ba), $(Me_5C_5)_2M(2,6\text{-xylylisocyanide})_2$, and $(Me_5C_5)_2M(PEt_3)$ (M = Ca, Sr, Ba) have also been obtained. The $(Me_5C_5)_2Be$ cannot be prepared from $(Me_5C_5)_2Mg$ and $BeCl_2(OEt_2)_2$; instead Me_5C_5BeCl is isolated.

The organometallic chemistry of the lighter alkaline earth metals is rather extensively developed, doubtless due to the synthetic utility of organomagnesium reagents [1]. In contrast, the organometallic chemistry of the heavier alkaline earths is rather scarcely developed [2]. In particular, the metallocene chemistry of calcium, strontium, and barium, $(C_5R_5)_2M$, is limited to reports on their synthesis [3], vibrational spectroscopy [4], and the X-ray crystal structure of Cp_2Ca [5]. The unsubstituted cyclopentadienyl compounds, $(C_5H_5)_2M$, are volatile (the sublimation temperatures vary from 260 to 440°C from Ca to Ba under reduced pressure) and form 1:2 coordination complexes with Lewis bases [3]. The base-free compounds are not soluble in hydrocarbon solvents, and Cp_2Ca is polymeric in the solid state [5]. The properties of the later alkaline earth metallocene are not dissimilar from those of the corresponding divalent lanthanide metallocenes of europium and ytterbium [6], and this is not unexpected since Ca^{II} and Yb^{II} are similar in size, as

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* This paper is dedicated to Professor G.E. Coates, a scholar, teacher, and gentleman, on the occasion of his 70th birthday, with gratitude and thanks.
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TABLE 1

PHYSICAL PROPERTIES AND ^{1}H NMR SPECTROSCOPIC DATA

Compound	M.p. ($^\circ$C)	^{1}H NMR (C_6D_6, 30°C)	
		Me_5C_5	Other resonances
$(Me_5C_5)_2Sr(OEt_2)$	210–215	2.07	2.82, (q, 4H, J 7 Hz)
			0.74 (t, 6H, J 7 Hz)
$(Me_5C_5)_2Ba(thf)_2$	187–191	2.12	3.33 (8H, m)
			1.33 (8H, m)
$(Me_5C_5)_2Sr$	216–218	1.95	
$(Me_5C_5)_2Ba$	265–268	1.97	
$(Me_5C_5)_2Ca(CNC_8H_9)_2$	213–215 (dec)	2.35	6.65 (6H, m)
			2.17 (12H, s)
$(Me_5C_5)_2Sr(CNC_8H_9)_2$	230–233 (dec)	2.38	
$(Me_5C_5)_2Ba(CNC_8H_9)_2$	211–212 (dec)	2.29	
$(Me_5C_5)_2Ca(PEt_3)$	111–113	1.98	1.21 (6H, m)
			0.87 (9H, m)
$(Me_5C_5)_2Sr(PEt_3)$	140–142	2.03	
$(Me_5C_5)_2Ba(PEt_3)$	250–255	1.96	

are Sr^{II} and Eu^{II} [7]. The permethylmetallocene derivative of ytterbium, $(Me_5C_5)_2Yb$, is volatile, soluble in aromatic and aliphatic hydrocarbons, and monomeric in the gas phase [8a] with a bent, C_{2v}, structure [8b]. Clearly coordination polymerization can be prevented by sterically bulky ligands. We have extended this strategy of using voluminous ligands to give compounds with low coordination numbers to the alkaline earth permethylmetallocenes, $(Me_5C_5)_2M$, which are soluble in hydrocarbons, volatile and monomeric in the gas phase with bent, C_{2v}, structures for M = Ca [8b] and M = Sr, Ba [8c]. The $(Me_5C_5)_2Yb$ compound gives 1 : 1 and 1 : 2 complexes with a variety of Lewis bases [9], and we thought it would be of interest to explore the coordination chemistry of $(Me_5C_5)_2M$, where M is Ca, Sr, or Ba. We chose to study the Lewis bases bipyridine (since this ligand usually gives colored complexes with alkaline earth organometallic compounds [10]), PEt_3 (since there are few phosphine complexes of the Group II metals [11]), and 2,6-xylylisocyanide (since no isocyanide complexes of these metals have been described).

The diethyl ether complex of strontium, $(Me_5C_5)_2Sr(OEt_2)$, was prepared by reaction of SrI_2 and two molar equivalents of NaC_5Me_5 in diethyl ether, as outlined previously for the calcium complex [8b]. The colorless complex may be crystallized from the mother liquor. Some physical properties for the complexes described in this paper are given in Table 1 and in the Experimental section. The corresponding barium complex cannot be prepared similarly since BaI_2 does not react at an appreciable rate with NaC_5Me_5 in diethyl ether, though reaction in tetrahydrofuran gives colorless needles of $(Me_5C_5)_2Ba(thf)_2$ which may be crystallized from toluene in high yield. The diethyl ether or tetrahydrofuran may be removed from the two complexes by exposing a refluxing toluene solution to vacuum for several hours, as previously outlined for the preparation base-free $(Me_5C_5)_2Ca$ [8b]. It is noteworthy that the method used to prepare the base-free permethylmetallocenes owes much to the method developed by Professor G.E. Coates to isolate base-free beryllium alkyls [12]. The base-free strontium and barium compounds are soluble in hydrocarbons and they sublime in vacuum at temperatures below 135°C. The barium compound

is very air- and moisture-sensitive, much more so than either the calcium or strontium compound, though all of the metallocenes may be stored in absence of air and water at room temperature for months. The compounds give monomeric molecular ions in the mass spectrum. The gas phase photoelectron spectra and electron diffraction data are consistent with a bent, C_{2v}, sandwich structure, similar to that of the calcium and ytterbium compounds [8c,d].

The base-free metallocenes of Ca, Sr, or Ba give 1:1 orange-red complexes with bipyridine. The complexes are not soluble enough in aromatic hydrocarbons to give satisfactory ^{1}H NMR spectra.

The phosphine complexes of all three permethylmetallocenes, $(Me_5C_5)_2M(PEt_3)$, can be isolated as colorless crystals from pentane or toluene. The ${}^{31}P\{^1H\}$ NMR spectra of all three complexes in benzene-d_6 at 30°C show a single resonance at δ -20.3 ± 0.2, very close to the chemical shift of free PEt_3, δ -20.4, under similar conditions. At $-80°C$ the ${}^{31}P\{^1H\}$ NMR resonance of the calcium compound in toluene-d_8 does not shift nor broaden but the resonances in the strontium and barium compounds shift to δ -21.7 and -21.8 and the resonances broaden slightly to $\nu_{1/2} = 4$ Hz. These observations are consistent with a chemical exchange process occurring on the ${}^{31}P$ NMR time scale which becomes detectably slow at $-80°C$ for the heavier two metallocenes but is still rapid in the case of calcium. The solution NMR data show that the metal phosphine interaction is weak, since the change in ${}^{31}P$ NMR average chemical shift on coordination is very small. Further, the barrier to chemical exchange is not large, since in no case was the exchange stopped at $-80°C$.

The isocyanide, 2,6-xylylisocyanide, gives yellow 1:2 complexes with all three metallocenes. The infrared spectrum for each compound shows two $\nu(CN)$ absorptions in the solid state, one of which is at higher frequency, 2145vs (Ca), 2150vs (Sr), 2138vs (Ba) than the other which is at 2115m cm^{-1} in each case. The latter is close to the $\nu(CN)$ for the free isocyanide, 2120 cm^{-1}, under comparable conditions. The 2115 cm^{-1} absorption could be due to some dissociation through two infrared active absorptions are predicted for the 1:2 complexes in idealized C_{2v} symmetry. The ^{1}H NMR spectra of these complexes show that chemical exchange processes, presumably ligand dissociations, are occurring in solution. At 30°C in benzene-d_6 the sharp ($\nu_{1/2} < 0.5$ Hz) resonances due to the methyl groups of the isocyanide are at δ 2.17 (Ca), 2.12 (Sr), 2.12 (Ba). These resonances broaden, $\nu_{1/2} = 10$–12 Hz, at $-80°C$ in toluene-d_8 and shift to δ 2.06 (Ca), 2.04 (Sr), 2.09 (Ba), though the slow exchange region is not reached. The chemical shift of the free ligand is δ 2.05.

It is of interest to compare the coordination chemistry of the Ca, Sr, and Ba permethylmetallocenes with that of the lighter analogues. The $(Me_5C_5)_2Mg$ derivative yields a 1:1 complex with bipyridine that is red-purple and only sparingly in hydrocarbon solvents. No coordination complexes could be isolated with PMe_3 or 2,6-xylylisocyanide. This result is readily rationalized on the basis of steric effects, caused by bending the bulky Me_5C_5 groups towards each other in order to allow the ligand space to coordinate to the metal center, since the unsubstituted metallocene, Cp_2Mg, has a rather rich coordination chemistry [13].

We have not been able to extend this chemistry to the lightest Group II element, beryllium, since we have been unable to prepare $(Me_5C_5)_2Be$. Reaction of $(Me_5C_5)_2Mg$ or NaC_5Me_5 with $BeCl_2 \cdot 2OEt_2$ gives the one ring compound $(Me_5C_5)BeCl$, which is very soluble in pentane and is monomeric in gas phase by

mass spectroscopy. The structure is doubtless similar to that of the unsubstituted species CpBeCl [14].

Experimental

All operations were carried out under nitrogen. Analyses were carried out in the microanalytical laboratory of this department. The NMR spectra were recorded on a JEOL FX-90Q instrument operating at 89.56 MHz for proton, 36.25 MHz for phosphorus, and 22.50 MHz for carbon in deuterated benzene or toluene. Chemical shifts are expressed in δ-units relative to Me_4Si for ^1H and ^{13}C and relative to 85% H_3PO_4 for ^{31}P. Infrared spectra are recorded as Nujol mulls between CsI plates on a Nicolet FTIR machine. Mass spectra were determined by electron impact ionization on a AEI-MS-12 instrument equipped with a direct inlet.

$(Me_5C_5)_2Sr(OEt_2)$

Strontium diiodide (2.30 g, 6.74 mmol) [15] and NaC_5Me_5 (2.02 g, 12.8 mmol) [16] were stirred together in diethyl ether (200 ml) for 36 h. The solution was filtered, then the filtrate was concentrated to ca. 120 ml, and cooled to $-25°C$. The white needles were collected, and dried under reduced pressure. Two additional crops of needles were obtained from the mother liquor in a combined yield of 1.9 g (68%). We were unable to get satisfactory microanalytical data for this complex, presumably owing to its ready loss of ether. IR: 2722m, 1650wbr, 1488m, 1419m, 1159m, 1146s, 1079vs, 1038s, 1013m, 927m, 838s, 818w, 797w, 724wbr, 668w, 620wbr, 588m, 545wbr, 513w, 422w, 416w, 397w, 355mbr, 282vsbr cm^{-1}. ^{13}C NMR (C_6D_6, 31°C): δ 112.5 (s, C_5Me_5), 66.34 (t, J(CH) 143 Hz, OCH_2Me), 13.25 (q, J(CH) 127 Hz, OCH_2Me), 11.09 (q, J(CH) 125 Hz, C_5Me_5).

$(Me_5C_5)_2Ba(thf)_2$

Barium diiodide (2.60 g, 6.65 mmol) [15] and NaC_5Me_5 (2.10 g, 13.3 mmol) were stirred in tetrahydrofuran (200 ml) for 48 h. The tetrahydrofuran was removed under reduced pressure. The residue was dissolved in hot toluene (150 ml); the solution was filtered, and the volume of the filtrate was reduced to ca. 100 ml. Cooling ($-25°C$) produced white needles. Two more crops of needles were produced from the mother liquor in a combined yield of 2.8 g (75%). Anal. Found: C, 60.9; H, 8.54. $C_{28}H_{46}O_2Ba$ calc: C, 60.9; H, 8.40%. IR: 2723m, 1651wbr, 1496m, 1294w, 1285w, 1246m, 1212m, 1146w, 1129w, 1080m, 1037vs, 957w, 930w, 899vs, 859sh, 797mbr, 729m, 646w, 642w, 611mbr, 587sh, 466w, 419w, 404wbr, 362wbr, 308m, 282sh, 258vsbr cm^{-1}. ^{13}C NMR (C_6D_6, 30°C): δ 112.7 (s, C_5Me_5), 68.02 (t, J(CH) 146 Hz, OCH_2CH_2), 25.44 (t, J(CH) 134 Hz, OCH_2CH_2), 11.21 (q, J(CH) 123, C_5Me_5).

$(Me_5C_5)_2Sr$

The monoether complex, $(Me_5C_5)_2Sr(OEt_2)$ (1.50 g, 3.47 mmol) was dissolved in toluene (200 ml) in a greaseless Schlenk tube, the solution was heated to 100°C and the solvent was removed slowly (2–3 h) under vacuum. The toluene reflux procedure was repeated with additional toluene (200 ml). The residue was extracted with hexane (150 ml) and the volume of the extract was reduced to ca. 80 ml. Cooling ($-25°C$) afforded white blocks, which were collected and dried under reduced

pressure. An additional batch of crystals was obtained from the mother liquor in a combined yield of 1.1 g (88%). The compound sublimed at $100-110°C/10^{-3}$ mmHg. We have been unable to get satisfactory microanalytical data for this compound (or for the barium analogue), but its spectral data leave no doubt as to its identity. MS, molecular ion (observed intensity, calculated intensity): 359 (21.4, 22.0); 358 (100, 100); 357 (11.4, 10.9); 356 (12.1, 11.7). ^{13}C NMR (C_6D_6, 31°C): δ 113.6 (s, C_5Me_5), 10.83 (q, J(CH) 125 Hz, C_5Me_5). IR: 2725w, 1650wbr, 1244w, 1162w, 1148m, 1038m, 1020m, 956w, 721mbr, 737sh, 699sh, 668w, 631w, 620w, 589w, 546w, 516w, 430w, 396w, 366w, 354m, 308sh, 289vsbr cm^{-1}.

$(Me_5C_5)_2Ba$

This compound was prepared from $(Me_5C_5)_2Ba(thf)_2$ by the toluene-reflux method by a procedure similar to that used to prepare $(Me_5C_5)_2Sr$, and crystallized as white needles from toluene in 85% yield. The base-free compound sublimed slowly at $130-140°C/10^{-3}$ mmHg. MS: molecular ion, 410 (2.26, 2.30); 409 (27.2, 21.9); 408 (100, 100); 407 (17.0, 17.6); 406 (15.3, 12.7); 405 (11.0, 9.59); 404 (2.90, 3.23). IR: 2723m, 1653wbr, 1497sh, 1342sh, 1309w, 1290w, 1148w, 1030m, 1019m, 1004sh, 941w, 929w, 860wbr, 775w, 728m, 719sh, 695w, 668w, 636w, 626w, 611w, 589w, 464w, 408wbr, 259vsbr cm^{-1}. ^{13}C NMR (C_6D_6, 31°C): δ 114.0 (s, C_5Me_5), 11.10 (q, J(CH) 124 Hz, C_5Me_5).

$(Me_5C_5)_2Ca(bipy)$

The base-free $(Me_5C_5)_2Ca$ (0.31 g, 1.0 mmol) [8] in hexane (30 ml) was added to bipyridine (0.16 g, 1.0 mmol) in hexane (10 ml). The solution turned red-purple and an orange-red precipitate formed. After 2 h stirring the precipitate was allowed to settle and was filtered off. The complex does not melt below 300°C. Anal. Found: C, 76.9; H, 8.27; N, 5.82. $C_{30}H_{38}N_2Ca$ calc: C, 77.2; H, 8.21; N, 6.00%. IR: 3059m, 2721m, 1598s, 1592s, 1575m, 1568m, 1490m, 1475s, 1436vs, 1312m, 1245w, 1224w, 1175w, 1156m, 1114w, 1103w, 1061w, 1043m, 1021sh, 1012s, 1000sh, 966w, 960sh, 892w, 881w, 813w, 759vs, 742m, 696w, 668w, 653w, 643m, 625m, 588w, 555w, 417w, 375sh, 350sh, 327vsbr, 288m cm^{-1}.

$(Me_5C_5)_2Sr(bipy)$

This orange-red compound was prepared by a procedure analogous to that used for the calcium analogue and its infrared spectrum was similar to that of the latter. Anal. Found: C, 69.4; H, 7.51; N, 5.38. $C_{30}H_{38}N_2Sr$ calc: C, 70.0; H, 7.46; N, 5.45%.

$(Me_5C_5)_2Ba(bipy)$

This orange-red compound was prepared in the way described for its calcium analogue, and the infrared spectrum was similar to that of the latter. Anal. Found: C, 63.0; H, 6.92; N, 4.96. $C_{30}H_{38}N_2Ba$ calc: C, 63.9; H, 6.80; N, 4.97%.

$(Me_5C_5)_2Mg(bipy)$

This red-purple compound was made in the way described for the calcium analogue, and its infrared spectrum was superimposable on that of the latter. Anal. Found: C, 79.2; H, 8.60; N, 6.00. $C_{30}H_{38}N_2Mg$ calc: C, 80.0; H, 8.44; N, 6.22%.

(Me₅C₅)₂M(2,6-xylylisocyanide)₂ (M = Ca, Sr, Ba)

All these complexes were prepared in the same way, their infrared spectra were similar, and the isocyanide resonances in their ^{1}H NMR spectra were identical, so only the procedure for the calcium complex is given. Base-free $(Me_5C_5)_2Ca$ (0.13 g, 0.42 mmol) in toluene (10 ml) was added to the isocyanide (0.11 g, 0.84 mmol) in toluene (20 ml) and the yellow solution was stirred for 30 min. The solution was reduced in volume to ca. 15 ml and cooled to −25°C. The yellow blocks were filtered off, and dried under reduced pressure. A second crop of blocks was isolated from the mother liquor in a combined yield of 0.18 g (75%). Anal. Found: C, 78.9; H, 8.54; N, 4.81. $C_{38}H_{48}N_2Ca$ calc: C, 79.7; H, 8.45; N, 4.89%. IR: 3066w, 2718m, 2145vs, 2115m, 1946w, 1870w, 1790w, 1671w, 1653sh, 1604sh, 1591w, 1552vw, 1488sh, 1443s, 1300w, 1273w, 1170s, 1150sh, 1098sh, 1085m, 1060w, 1036m, 1020m, 991w, 976w, 924w, 897m, 882sh, 803m, 777vs, 719s, 638w, 589w, 573w, 548w, 511w, 379s, 363s, 334vs, 283sbr cm^{-1}.

(Me₅C₅)₂Sr(2,6-xylylisocyanide)₂

Anal. Found: C, 73.3; H, 7.91; N, 4.49. $C_{38}H_{48}N_2Sr$ calc: C, 73.6; H, 7.80; N, 4.52%.

(Me₅C₅)₂Ba(2,6-xylylisocyanide)₂

Anal. Found: C, 65.8; H, 7.13; N, 4.20. $C_{38}H_{48}N_2Ba$ calc: C, 68.1; H, 7.23; N, 4.18%.

(Me₅C₅)₂M(PEt₃) (M = Ca, Sr, Ba)

All the complexes were prepared in the same way, so the details are given only for the calcium complex. The infrared spectra above 400 cm^{-1} and ^{1}H NMR spectra in the phosphine region were superimposable. Microanalytical data consistently gave low and erratic results for the strontium and barium complexes, probably because they readily lose phosphine ligand. Base-free $(Me_5C_5)_2Ca$ (0.14 g, 0.45 mmol) in pentane (15 ml) was added to triethylphosphine (0.070 ml, 0.47 mmol) in pentane (5 ml). After 10 min stirring the solution was filtered, and the volume of the filtrate was reduced to ca. 5 ml. Cooling to −25°C yielded white needles in 88% (0.17 g) yield. Anal. Found: C, 73.0; H, 10.7; P. 6.97. $C_{26}H_{45}PCa$ calc: C, 72.8; H, 10.6; P, 7.22%.

Me₅C₅BeCl

Magnesium bis(pentamethylcyclopentadienide) (3.2 g, 11 mmol) [17,8] in toluene (50 ml) was added to $BeCl_2(OEt_2)_2$ (5.0 g, 22 mmol) in diethyl ether (75 ml) and the mixture was refluxed for 12 h then cooled to room temperature. The volatile material was removed under reduced pressure and the residue extracted with pentane (100 ml). The extract was filtered, then concentrated to ca. 30 ml. Cooling to −10°C afforded large colorless needles that were further purified by sublimation at 50–60°C/10^{-2} mmHg. The yield was 2.1 g (54%), m.p. 109–110°C. Anal. Found: C. 67.0; H, 8.27. $C_{10}H_{15}BeCl$ calc: C, 66.9; H, 8.36%. MS: molecular ion, 182 (3.26, 3.63); 181 (30.9, 33.0); 180 (29.4, 11.1); 179 (100, 100). IR: 2730w, 1056s, 1020m, 913sbr, 799m, 724m, 509w, 385s cm^{-1}. ^{1}H NMR (C_6D_6, 31°C): δ 1.67.

Acknowledgement

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