Journal of Organometallic Chemistry, 55 (1973) 229–235

THE ORGANOMETALLIC CHEMISTRY OF THE ALKALINE EARTH METALS

I. SOME CHEMICAL AND SPECTROSCOPIC PROPERTIES OF DICYCLOPENTADIENYLCALCIUM

K. A. ALLAN, B. G. GOWENLOCK and W. E. LINDSELL
Chemistry Department, Heriot-Watt University, Edinburgh, EH1 1HX (Great Britain)
(Received October 31st, 1972)

SUMMARY

Some properties of dicyclopentadienylcalcium have been investigated. The compound has been shown to form complexes with nitrogen or oxygen donor ligands of the general formula $(C_5H_5)_2CaL_2$ (where L=pyridine or L_2=*N,N,N',N'*-tetramethylethylenediamine, 2,2'-bipyridine or 1,2-dimethoxyethane). When L_2= 1,10-phenanthroline a solvated complex $(C_5H_5)_2CaL_2 \cdot n$(tetrahydrofuran) or a complex of composition $(C_5H_5)_2Ca(L_2)_2 \cdot n$(pyridine), n=0.5–2, is obtained. The ^1H NMR and IR spectra of these products have been studied.

Dicyclopentadienylcalcium has also been shown to be a useful cyclopentadienylating reagent, which readily forms cyclopentadienyl compounds on reaction with metal halides.

INTRODUCTION

In contrast to the metals magnesium and beryllium, the other Group IIA metals, calcium, strontium and barium, have been shown to form few isolable, characterised organometallic compounds. The first such reported compound of calcium was dicyclopentadienylcalcium which has been formed by reaction of cyclopentadiene with the metal, the metal carbide or the metal hydride[1,2]. In recent publications a limited number of other characterised organocalcium compounds have been described, including the triphenylmethyl derivatives, $(C_6H_5)_3CCaCl$[3] and $[(C_6H_5)_3C]_2Ca$[4], bis(2-phenylethynyl)calcium[5] and di-*p*-tolylcalcium[6].

Few studies of the chemical or spectroscopic properties of these compounds have been carried out. Dicyclopentadienylcalcium has been shown to form a complex of composition $(C_5H_5)_2Ca(C_4H_8O)_2$ with tetrahydrofuran[2] and a solvate with ammonia[1]. It is rapidly hydrolysed and forms dicyclopentadienyl dicarboxylic acid on carbonation[1]. The IR spectrum of dicyclopentadienylcalcium has also been reported and discussed[2,7]. We have investigated further properties of this compound.

RESULTS AND DISCUSSION

Dicyclopentadienylbis(tetrahydrofuran)calcium, (I), was prepared by reaction of calcium metal with cyclopentadiene in tetrahydrofuran, and free dicyclopentadienylcalcium, (II), was obtained by sublimation of (I) under high vacuum. Complexes of the general formula $(C_5H_5)_2CaL_2$ [where L_2 = 1,2-dimethoxyethane, (III); L_2 = *N,N,N',N'*-tetramethylethylenediamine, (IV); L = pyridine, (V) and L_2 = 2,2'-bipyridine, (VI)] were formed as crystalline solids by reaction of (I) with the oxygen or nitrogen bonding ligand. These complexes, (III)–(VI), were characterised by analysis and integration of their ^1H NMR spectra. Some of their properties are listed in Table 1.

Complexes (III)–(VI) are soluble in tetrahydrofuran, pyridine and 1,2-dimethoxyethane and slightly soluble in ether, but in some cases it is probable that the coordinating solvent displaces L_2 from $(C_5H_5)_2CaL_2$. The solids are more stable to decomposition by air than (II), but are readily hydrolysed and show relatively low decomposition points *in vacuo*.

Reaction of (I) with 1,10-phenanthroline gave rise to several products containing coordinated ligand, but none had the simple formula $(C_5H_5)_2CaL_2$ (L_2 = 1,10-phenanthroline). Analysis of the calcium content and ^1H NMR spectra indicated that solvent molecules, tetrahydrofuran or pyridine, were also present. These solvent molecules could not be completely removed under high vacuum. The approximate compositions of two products were $(C_5H_5)_2Ca(C_{12}H_8N_2)\cdot n$THF, (VIIa), (THF = tetrahydrofuran, $n = 0.5$–2) and $(C_5H_5)_2Ca(C_{12}H_8N_2)_2\cdot n$Py, (VIIb), (Py = pyridine, $n = 1$–2). Complex (VIIb) is noticeably more stable to decomposition by air than the other complexes, and the calcium ion may have a higher coordination number in this case.

Attempts to prepare complexes of dicyclopentadienylcalcium with phosphine ligands proved unsuccessful. Thus, using tetrahydrofuran as a solvent, the reaction of (I) with an excess of 1,2-bis(diphenylphosphino)ethane led only to the isolation of unreacted (I).

Compound (I) is an efficient cyclopentadienylating agent, and reacts readily in polar organic solvents with metal halides, even at room temperature. Thus anhydrous ferrous chloride, titanium tetrachloride or mercuric chloride in 1,2-dimethoxyethane gave high yields of the corresponding dicyclopentadienyl compound, $(C_5H_5)_2Fe$, $(C_5H_5)_2TiCl_2$ or $(C_5H_5)_2Hg$. Reaction of (I) with hexacarbonyltungsten in refluxing tetrahydrofuran did not give the salt of the cyclopentadienyltricarbonyltungsten anion as does the analogous reaction with cyclopentadienylsodium. A low yield of an insoluble orange compound was obtained after prolonged refluxing of (I) with $W(CO)_6$ in THF. This product contained calcium and tungsten. Its IR spectrum indicated the presence of carbonyl and the absence of cyclopentadienyl groups but also suggested carbonato groups which were confirmed by analysis. These could be formed by ether cleavage and base attack at the carbonyl groups.

In an attempt to make the organocalcium halide, C_5H_5CaCl, analogous to the known magnesium derivative[8,10], a stoichiometric quantity of hydrogen chloride in 1,2-dimethoxyethane was added to a solution of (I). The products obtained from the reaction mixture were insoluble calcium chloride in quantitative yield and unreacted (I). It appears that in this solvent the equilibrium:

$$(C_5H_5)_2Ca + CaCl_2 \rightleftarrows 2\,C_5H_5CaCl$$

lies well to the left, and is controlled by the insolubility of calcium chloride.

Spectroscopic studies

Infrared spectra. The more intense bands in the IR spectra of complexes (I)–(VI) in the solid state are reported in the experimental section. The spectrum of (II) has been reported[2,7] and our data correlate fairly well with previous results. Fritz[7] concluded that the spectrum shows $(C_5H_5)_2Ca$ to be essentially an ionic compound since the band, γ(CH), 1119 cm^{-1} is weak and the bands, ν(C–C), 1433 cm^{-1}, and γ(C–H), 750 cm^{-1}, are close to the corresponding frequencies of C_5H_5K, *i.e.* 1446 and 712 cm^{-1}. Our frequencies for (I), 1122, 1437 and 751 cm^{-1}, are in agreement with this but they do not appear to differ significantly from those of $(C_5H_5)_2Mg$ —1108, 1428, 758 cm^{-1}—and the latter compound was described as "centrally σ-bonded"[7]. A band at 284 cm^{-1} is probably a skeletal vibration of dicyclopentadienylcalcium and may be either a (Ca–ring) tilt or ν(Ca–ring) asymmetric and if so this shows that the Ca–ring bond is relatively weak compared to Mg–ring bond in $(C_5H_5)_2Mg$[7] [ring tilt 526 cm^{-1}, ν(Mg–ring) 439 cm^{-1}].

The bands assignable to C_5H_5 ligands in complexes (I) and (III)–(VII) are comparable to those of (II). The γ(CH) vibrations in the region 700–800 cm^{-1}, see Table 1, are lower than those of uncoordinated (II) and suggest that the C_5H_5 ring is more ionic in these complexes.

Ligand vibrations give an indication of the strength of the Ca–O or Ca–N bonds. For complexes (I) and (III) bands assignable to ν(C–O–C) occur at 1032 and 1065 cm^{-1} respectively compared to the free ligand values (1070 cm^{-1} THF, 1112 cm^{-1} 1,2-dimethoxyethane). The shifts of ca. 40 cm^{-1} indicate a significant but relatively weak Ca–O interaction as shifts of 40–100 cm^{-1} are usually observed[9]. Small shifts are also noted for frequencies of the coordinated *N,N,N′,N′*-tetramethylethylenediamine, pyridine, 2,2′-bipyridine and 1,10-phenanthroline in complexes (IV), (V), (VI) and (VII). This supports coordination albeit weaker than in related transition metal complexes.

In compound (VIIa) the band assignable to ν(C–O–C) of tetrahydrofuran (1070 cm^{-1}) is not displaced from that of the free ligand so that the additional solvent molecules are probably uncoordinated in the lattice.

^1H nuclear magnetic resonance spectra. Dicyclopentadienylmagnesium in tetrahydrofuran shows a singlet C_5H_5 resonance at 4.18 τ which is not concentration dependent whereas resonances for $(C_5H_5)Na$, 4.29 τ at infinite dilution, and $(C_5H_5)Li$, 4.31 τ, 0.01 *M*, vary over a range of ca. 0.15 ppm with concentration[10]. The C_5H_5 resonance of (I) in tetrahydrofuran is comparable with that of $(C_5H_5)_2Mg$ and indicates a similar ionic charge on the C_5H_5 rings.

The ^1H NMR of complexes (I) and (III)–(VII) are recorded in Table 1. In solvents other than the coordinated ligand integration gives the composition of the solid complexes. Since the solvents are coordinating, however, it is uncertain whether the oxygen or nitrogen ligand present in the solid state remains bound to the calcium in solution.

In the case of complex (I) in pyridine or complex (V) in tetrahydrofuran the coordinated tetrahydrofuran or pyridine, respectively, is displaced by solvent.

TABLE 1

Compound		M.p (°C)	Colour	^1H NMR(τ)		IR (cm^{-1}) [C_5H_5 = γ(CH
				C_5H_5	Other	
(I)	$(C_5H_5)_2Ca(C_4H_8O)_2$[a]	dec. > 100	Colourless	(i) 4.25[c] (ii) 3.71[d]	[b] 6.37, 8.37	753, 727
(III)	$(C_5H_5)_2Ca(C_4H_{10}O_2)$	dec. > 100	Colourless	(i) 3.72[d] (ii) 4.22[e]	6.56, 6.79 [b]	752, 740
(IV)	$(C_5H_5)_2Ca(C_6H_{16}N_2)$	dec. > 360	Pale pink	(i) 3.78[d]	7.65, 7.86	754, 726
(V)	$(C_5H_5)_2Ca(C_5H_5N)_2$	168 (dec.)	Colourless	(i) 4.27[c]	1.44, 1.51, 2.35, 2.67, 2.77	749 [b]
(VI)	$(C_5H_5)_2Ca(C_{10}H_8N_2)$	229	Pale yellow	(i) 4.22[c]	1.47, 1.61, 2.19, 2.71	743[f], 718[f]
(VIIa)	$(C_5H_5)_2Ca(C_{12}H_8N_2)\cdot nC_4H_8O$[g]	dec. ≈ 100	Yellow	(i) 3.80[d]	0.96, 1.56. 1.69, 2.16, 2.4 (6.36, 8.39; C_4H_8O)	744, 713[f]
(VIIb)	$(C_5H_5)_2Ca(C_{12}H_8N_2)_2\cdot mC_5H_5N$[g]	dec. ≈ 80	Orange	(i) 3.80[d]	0.86, 1.65, 1.79, 2.20, 2.4, (+C_5H_5N resonances)	747, 713[f]

[a] Previously reported compound: see ref. 2. [b] Obscured by other bands. [c] In tetrahydrofuran. [d] In pyridine-d_5; [e] In 1 dimethoxyethane. [f] Uncertain since close to other ligand frequencies. [g] $n = 0.5–1$, $m = 1–2$.

Complex (I) was dissolved in pyridine/tetrahydrofuran mixtures of volume compositions 1/0, 2/1, 1/1, 1/2 and 0/1 and the respective resonances of the C_5H_5 singlet were 3.71, 3.87, 3.96, 4.06 and 4.25 τ. The difference in chemical shift for ferrocene in tetrahydrofuran (5.87 τ) and pyridine (5.82 τ) under similar conditions is very small so that the effect for dicyclopentadienylcalcium cannot be from the bulk medium and must arise from specific interaction between polar solvent and solute. Assuming the composition of the complexes in solution in pure pyridine or tetrahydrofuran to be respectively $(C_5H_5)_2Ca(NC_5H_5)_x$ or $(C_5H_5)_2Ca(OC_4H_8)_x$ where x is probably the same in each case and possibly, in the inner coordination sphere, $x = 2$, then the processes occurring in the mixed solvents are represented by the equilibria:

$$(C_5H_5)_2Ca(NC_5H_5)_x \underset{\text{Py}}{\overset{\text{THF}}{\rightleftharpoons}} (C_5H_5)_2Ca(OC_4H_8)(NC_5H_5)_{x-1} \underset{\text{Py}}{\overset{\text{THF}}{\rightleftharpoons}} \ldots$$

$$\ldots \underset{\text{Py}}{\overset{\text{THF}}{\rightleftharpoons}} (C_5H_5)_2Ca(OC_4H_8)_x$$

Here x may equal 2 and the chemical shifts increase for complexes from left to right.

Complex (VI), in tetrahydrofuran, shows a C_5H_5 resonance at a similar field as (I) and ligand resonances are only slightly shifted ($\leqslant 0.05$ ppm) from the resonances of the free ligand in the same solvent.

In general C_5H_5 resonances are singlets and no change was observed for complex (I) when the temperature was lowered to −40° in pyridine or −70° in 1,2-dimethoxyethane. A broadening, however, occurred when (I), in triethylamine, was lowered to −100°.

The compositions of the 1,10-phenanthroline complexes, (VIIa) and (VIIb) were obtained mainly from NMR results and the ligand resonances were shifted from those of free phenanthroline in the same solvent (pyridine-d_5) by up to 0.3 τ suggesting metal–ligand interaction.

EXPERIMENTAL

Calcium grain was finely ground in a steel mill under dry argon and stored under the same. Cyclopentadiene was prepared by pyrolysis of the dimer, dried over 5A molecular sieves and distilled immediately before use. Tetrahydrofuran and 1,2-dimethoxyethane were dried with lithium aluminium hydride. Pyridine and *N,N,N'*,-*N'*-tetramethylethylenediamine were dried with the minimum amount of phenyllithium. 1,10-Phenanthroline was purified by repeated sublimation under vacuum.

Calcium was determined by EDTA titration. IR spectra were recorded in KBr with a Perkin–Elmer 457 spectrometer and ^{1}H NMR spectra with a 60 MHz Perkin–Elmer R12 spectrometer operating at 37° unless otherwise stated. Melting points were determined in evacuated 1 mm tubes and are uncorrected.

All reactions were carried out under argon prepurified by passage through a column of B.T.S. catalyst at 200° and then through a column of 5 A molecular sieves.

Dicyclopentadienylbis(tetrahydrofuran)calcium (I)

This was prepared by reaction of cyclopentadiene with calcium metal in tetrahydrofuran according to the method of Fischer and Stölzle[2]. C_5H_6 (11.2 g) gave $(C_5H_5)_2Ca(C_4H_8O)_2$, (9.8 g), 37%. (Found: Ca, 12.6. $C_{18}H_{26}CaO_2$ calcd.: Ca, 12.7%). Major IR bands: 3078 m, 2970 m, 2878 m, 1032 s, 1009 s, 877 m, 753 vs, 727 s, 291 m cm^{-1}.

Free dicyclopentadienylcalcium was prepared by sublimation of (I) at 250° under high vacuum. IR: 3078 m, 2693 vw, 2406 vw, 1437 vw, 1367 vw, 1351 vw, 1122 vw, 1053 w, 1009 s, 891 vw, 872 w, 843 w, 807(sh), 780 s, 751 vs, 726 (sh), 664 vw, 627 w, 284 m cm^{-1}.

Dicyclopentadienyl(1,2-dimethoxyethane)calcium

The compound (I) (0.6 g) was dissolved in 1,2-dimethoxyethane (15 ml) at 40° and the solution was filtered and cooled slowly to −70°. The colourless crystals that formed were separated washed and dried for 30 min, 20°, 10^{-3} mmHg. (Found: Ca; 15.4. $C_{14}H_{20}CaO_2$ calcd.: Ca, 15.4%) Major IR bands: 3077 m, 1473 m, 1460 m, 1449 m, 1194 m, 1065 s, 1005 m, 855 m, 752 s, 740 vs, 305 m, 290 m cm^{-1}.

Dicyclopentadienyldipyridinecalcium

The compound (I) (0.6 g) was dissolved in a 1/2 solution (10 ml) of pyridine in tetrahydrofuran. Evaporation to 5 ml and cooling to −50° gave colourless crystals which were washed at −50° with the mixed solvent and dried, 1 h, 20°, 10^{-3} mmHg. (Found: Ca, 12.1. $C_{20}H_{20}CaN_2$ calcd.: Ca, 12.2%. Major IR bands: 3075 m, 1597 s, 1487 m, 1442 s, 1215 s, 1066 m, 1036 m, 1008, s 1003 s, 749 vs, 733 (sh), 701 s, 617 m, 411 w, 291 m cm^{-1}.

Dicyclopentadienyl (N,N,N',N'-tetramethylethylenediamine) calcium

The compound (I) was dissolved in a 1/2 solution of *N,N,N',N'*-tetramethylethylenediamine in tetrahydrofuran and cooled slowly to −60°. Isolation as above gave pale pink crystals. (Found: Ca, 13.7. $C_{16}H_{26}CaN_2$ calcd.: Ca, 14.0%.) Major IR bands: 3064 m, 2835 m, 1471 s, 1464 s, 1289 m, 1027 m, 1014 s, 1005, 950 m, 754 vs, 739 s, 726 vs, 290 m cm^{-1}.

Dicyclopentadienyl (2,2'-bipyridine) calcium

The compound (I) (0.5 g) was dissolved in tetrahydrofuran (15 ml) and bipyridine (0.25 g) was added while shaking. The solution became bright yellow and evaporation to 8 ml followed by cooling to −40° gave pale yellow crystals which were collected, washed and dried 20°, 10^{-3} mmHg. (Found: Ca, 12.2. $C_{20}H_{18}CaN_2$ calcd.: Ca, 12.3%.) Major IR bands: 3075 m, 1600 s, 1593 s, 1581 m, 1561 m, 1478 s, 1437 vs, 1422 m, 1317 s, 1153 s, 1009 s, 763 vs, 743 vs, 718 s, 293 m cm^{-1}.

Reaction of 1,10-phenanthroline with dicyclopentadienylbis(tetrahydrofuran)calcium

(*a*). 1,10-Phenanthroline (0.24 g) in tetrahydrofuran (10 ml) was added dropwise to a continuously agitated solution of compound (I) (0.4 g) in tetrahydrofuran. The yellow precipitate formed was separated from solution and washed with the minimum of tetrahydrofuran and dried 20°, 10^{-3} mmHg. (Found 10.0% Ca.)

(*b*). In a similar manner to above 1,10-phenanthroline (0.68 g) and compound (I) (0.4 g) gave an orange precipitate which was recrystallised from pyridine, washed and dried. (Found 6.2% Ca, 5.8% Ca.)

Reaction of metal halides with dicyclopentadienylbis(tetrahydrofuran)calcium

Slow addition of the metal halide ($TiCl_4$) or of the metal halides ($FeCl_2$ or $HgCl_2$) in dimethoxyethane to a stoichiometric amount of compound (I) in dimethoxyethane and subsequent reaction under the conditions outlined below gave the following yields of pure, isolable product, identified by melting point and IR and NMR spectroscopy:

a. $TiCl_4$: 2 h, 0°, $(C_5H_5)_2TiCl_2$, 87%;
b. $FeCl_2$: 1 h, reflux, $(C_5H_5)_2Fe$, 94%;
c. $HgCl_2$: 10 min, room temp., $(C_5H_5)_2Hg$, 95%.

Reaction of dicyclopentadienylbis(tetrahydrofuran)calcium with hydrogen chloride

A solution of hydrogen chloride in tetrahydrofuran (0.07 *M*, 3.3 ml) was added dropwise to a well stirred solution of (I) (0.7 g) in tetrahydrofuran (15 ml) at 20°. A white precipitate formed which was separated from solution by filtration at −20° and identified as a tetrahydrofuran adduct of calcium chloride. The filtrate was reduced to 5 ml *in vacuo* and cooled to −50° to give colourless crystals of unreacted (I) identified by analysis and by its IR spectrum. A test for chloride ion on the filtrate proved negative.

ACKNOWLEDGEMENT

We thank the International Synthetic Rubber Co. Ltd. for a grant in support of these investigations.

REFERENCES

1 K. Ziegler, H. Froitzheim-Kühlhorn and K. Hafner, *Chem. Ber.*, 89 (1956) 434.
2 E. O. Fischer and G. Stölzle, *Chem. Ber.*, 94 (1961) 2187.

3 R. Masthoff and G. Krieg, *Z. Chem.*, 6 (1966) 433.
4 M. A. Coles and F. A. Hart, *Chem. Ind. (London)*, (1968) 423.
5 M. A. Coles and F. A. Hart, *J. Organometal. Chem.*, 32 (1971) 279.
6 K. A. Kocheshkov, I. E. Paleeva, N. I. Sheverdina and M. A. Zemlyanichenko, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1970) 1921.
7 H. P. Fritz and R. Schneider, *Chem. Ber.*, 93 (1960) 1171.
8 C. Johnson, J. Tovey and G. D. Stucky, *J. Organometal. Chem.*, 40 (1972) C11.
9 K. Nakamoto, *Infrared spectra of inorganic and coordination compounds*, 2nd ed., 1970.
10 W. T. Ford, *J. Organometal. Chem.* 32 (1971) 27.