coordinated oxygen atoms to the ligand field potential is inversely proportional to its distance from the cobalt ion, we may select "centers of gravity" of the electrostatic potential on each of the four A–B lines (Figure 2). It is found that these four points define a bisphenoid with an average vertical angle of 107°, that is, very nearly a regular tetrahedron. In this way, the "tetrahedral mimicry" in the spectral and magnetic properties is very neatly explained. This viewpoint is qualitatively similar to that previously proposed[5,6] for the $Co(OMR_3)_2(NO_3)_2$ complexes.

Discussion of the High Coordination Number.—There does not appear to be any other case in which Co(II) has a coordination number of eight, and it is therefore of interest to consider whether there are any special features of the present situation which are responsible for its occurrence here.

We believe that the most important factor is that, because of the internal structure of the nitrate ion, four of the O · · · O distances are very short (~2.1 A). It is therefore possible to fit such a large number of oxygen atoms around the cobalt ion, keeping the other O · · · O contacts at or near the normal sum of the nonbonded radii while simultaneously maintaining close Co–O distances. We may add to this observation the one made earlier, namely, that the mean positions of the close pairs of ligand atoms lie approximately at the vertices of a tetrahedron, which is one of the common coordination polyhedra for the metal ion concerned.

There would seem to be no reason why such a combination of structural features could not occur with other metal ions, and, in fact, several other examples may be cited.

With the nitrate ion itself, there is the nearly isostructural $Ti(NO_3)_4$ molecule, recently described by Addison, *et al.*[17] Even more interesting, because it represents the same principles operating in the framework of a different and higher set of coordination numbers, is the structure of $Mg_3Ce_2(NO_3)_{12} \cdot 24H_2O$,[18] in which each Ce(IV) ion is surrounded by six bidentate nitrate ions. The oxygen atoms lie at the vertices of a distorted icosahedron, and the actual coordination number of the ceric ion is 12, a rather high value for an ion of radius ~0.9 A. In this case, the midpoints of the intranitrate O · · · O lines lie approximately at the vertices of an octahedron, a common coordination polyhedron.

The structures of several peroxo complexes might also be mentioned, most notably that of the $[Cr(O_2)_4]^{3-}$ ion,[19] which has a D_{2d} structure very much like those of $[Co(NO_3)_4]^{2-}$ and $Ti(NO_3)_4$. Again, the fact that some interligand distances are constrained to be very short (~1.4 A) permits a high coordination number (the Cr(V) ion must be quite small for a coordination number of eight) and the mean positions of the close pairs of ligand atoms approximately define a common coordination polyhedron (a tetrahedron) corresponding to a more normal coordination number for the ion in question.

It seems reasonable to expect that the principles manifested in the $[Co(NO_3)_4]^{2-}$ structure and the others just cited should also be exemplified in other compounds and that they might serve to design some new complexes with high coordination numbers.

Acknowledgments.—We thank the M.I.T. Computation Center for generous allotments of time on the IBM 7090 and 7094 computers, and we gratefully acknowledge helpful discussions with Dr. John S. Wood.

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(17) C. C. Addison, C. D. Garner, W. B. Simpson, D. Sutton, and S. C. Wallwork, *Proc. Chem. Soc.*, 367 (1964).

(18) A. Zalkin, J. D. Forrester, and D. H. Templeton, *J. Chem. Phys.*, **39**, 2881 (1963).

CONTRIBUTION FROM THE DIVISION OF MINERAL CHEMISTRY AND THE DIVISION OF ORGANIC CHEMISTRY,
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The Reaction of Molten Magnesium Cyclopentadienide with Fluorides and Other Metal Halides

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Molten magnesium cyclopentadienide in the absence of solvent reacts with a large number of metal halides, and in particular fluorides, to give cyclopentadienyl metal compounds, frequently in good yield. The reaction is particularly suited to the preparation of the cyclopentadienyls of thorium, uranium, scandium, and the rare earths from their fluorides, which are readily accessible and relatively stable to moisture.

Introduction

Magnesium cyclopentadienide ($MgCp_2$) is a readily sublimable white solid which melts at 177° to a clear, mobile liquid boiling at 222°.[1] Although it is thermodynamically somewhat more stable than ferrocene, the high free energies of formation of the magnesium

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(1) H. S. Hull, A. F. Reid, and A. G. Turnbull, *Australian J. Chem.*, **18**, 249 (1965).

halides will in principle allow the reaction of $MgCp_2$ with any halides other than those of the alkali metals and some of the alkaline earths.

The preparation of several metallocenes from anhydrous metal chlorides and $MgCp_2$ in solution has been reported.[2] This paper describes the reactions of molten $MgCp_2$ with a range of anhydrous halides, in particular, fluorides, in the absence of solvent.

Experimental Section

General.—All weighings of air-sensitive compounds were performed on a balance in an evacuable argon-filled drybox fitted with an evacuable lock. Air-sensitive compounds were generally transferred in the drybox, but were also manipulated under nitrogen or in a vacuum system using glass break-seals.

Metal Chlorides.—$AlCl_3$, $FeCl_3$, $PbCl_2$, and also PCl_3 were reagent grade chemicals, taken from freshly opened containers. $PbCl_2$ was air dried at 110°. The chlorides $CoCl_2$, $CrCl_3$, $FeCl_2$, $MnCl_2$, $MoCl_5$, $NbCl_5$, $NiCl_2$, $TiCl_3$, VCl_3, and WCl_6 were prepared by various methods published in *Inorganic Syntheses*, care being taken in all cases to avoid atmospheric contamination. Reagent grade $TiCl_4$ was redistilled over copper turnings, and $ZrCl_4$, prepared by the reaction of chlorine with zirconium turnings[3] at 700°, was purified by vacuum sublimation.

Metal Fluorides.—CeF_4 was prepared by fluorination of CeO at 500°;[4] ScF_3 and CeF_3 were prepared by hydrofluorination of Sc_2O_3 at 700° and CeO_2 at 500°.[5] ThF_4, UF_4, and ZrF_4 were prepared by dehydration of the hydrated salts in a stream of anhydrous HF at 400–500°.[5] NdF_3 and SmF_3 were precipitated from an alcoholic solution of the nitrates by addition of 40% hydrofluoric acid solution,[6] washed with alcohol and ether, and dried under vacuum. PbF_2 was reagent grade material, dried under vacuum at 250°.

Bromides and Iodides.—$ZrBr_4$ and ZrI_4 were prepared by the reactions under vacuum of bromine and iodine, respectively, with zirconium metal turnings. SmI_2 was made by vacuum disproportionation of ammonium samarium iodide hydrate first at 200°, then at 430°.[7]

Magnesium Cyclopentadienide.—Crystalline magnesium cyclopentadienide was prepared by an adaption[2] of the method of Barber.[8] In laboratory preparations the loose solid is conveniently weighed out in an inert atmosphere box, but it can be sublimed or melted into weighed or graduated vessels. Sublimation at 150° through ground joints lubricated with silicone high-vacuum grease can easily be carried out.

On a larger scale the molten material can be run through heated pipelines and is inert to glass, Teflon, steel, copper, aluminum, and brass.

Reaction Procedure.—Reactions were generally carried out in glass tubes 1.5 cm in diameter and 10–12 cm in length fitted with a spherical break-seal. $MgCp_2$ (2.0 g), anhydrous metal halide (sufficient for stoichiometric reaction), and 10–20 0.125-in. glass beads were placed in the tube in the glove box. After sealing under argon, the tube was placed inside a longer glass tube and held in place with asbestos packing. The larger tube was now rotated, *via* a flexible connection to a small motor, at 50–80 rpm inside a furnace heated to 180–280°. The tumbling action and the presence of glass beads served to mix the slurry of molten $MgCp_2$ and solid metal halide during reaction.

In attempts to increase the yield of ferrocene by this procedure, finely ground $FeCl_2$ (8 g) and $MgCp_2$ (10 g) were milled continuously in a larger version of this reaction tube 4 cm in diameter and one-third filled with glass beads. The reaction of crystalline ferrous chloride soon slowed, and even with finely divided $FeCl_2$, prepared by grinding in the absence of air or by dehydration of hydrated ferrous chloride with thionyl chloride, reaction was only 30–40% complete after 6–20 hr at 250–280°. Use of an excess of molten $MgCp_2$ had little effect. This is possibly due to the isomorphism of $MgCl_2$ with $FeCl_2$, their closely similar unit cell dimensions[9] allowing a coherent layer or solid solution of $MgCl_2$ on the surface of the $FeCl_2$ particles.

In the preparation of cyclopentadienylmanganese tricarbonyl, manganese dichloride (8 g) and magnesium cyclopentadienide (10 g) were weighed, either into a glass liner of a 450-ml Parr bomb or directly into the bomb. The latter procedure was preferable, as use of the liner allowed segregation of the reactants during heating of the bomb and thus lowered yields. The bomb was evacuated *via* its gas couplings, filled with CO to a pressure of 800 psi, and heated at 220° with rocking, for 12–15 hr. In one instance 20 ml of dry tetrahydrofuran (THF) was added before pressurizing, and in this case the reaction temperature was 150°.

The reactions of $NbCl_5$, $TaCl_5$, $MoCl_5$, and WCl_6 with $MgCp_2$ were violent, initiating at 100–120°. Reactions were eventually performed in a stainless steel tube sealed with a Teflon gasket and in each case produced dark brown or black, finely divided reaction products containing no unreacted $MgCp_2$.

Separation Procedures.—The bis(cyclopentadienyl) derivatives of Co, Cr, Mn, and V were not separated from the unreacted $MgCp_2$ but were cosublimed, and the amount of metal present was determined by standard titration methods after hydrolysis of the sublimate.

Ferrocene was separated by dissolution of the reaction mixture with methylene dichloride, which destroys excess $MgCp_2$,[2] filtration, evaporation of the solvent, and sublimation of the product. Cyclopentadienylmanganese tricarbonyl was similarly separated and purified.

Bis(cyclopentadienyl)lead was separated from the more volatile magnesium compound by vacuum sublimation along a heated tube, while the cyclopentadienyl derivatives of Ce, Nd, Sc, Sm, Th, Ti(III), and U, and also bis(cyclopentadienyl)-zirconium(IV) iodide, were freed of excess $MgCp_2$ by heating under vacuum at 100–120° and then sublimed from the reaction residue at 170–220°. Except for the thorium and uranium tetrakis(cyclopentadienyls), all of the latter group of compounds sublimed onto a cold finger or down a tube without decomposition.

Tetrakis(cyclopentadienyl)thorium sublimes with 1–2% of a hydrocarbon decomposition product[10] and must be finally purified by washing with petroleum ether (bp 40–60°). It is, however, air stable. Tetrakis(cyclopentadienyl)uranium was found to decompose partly on sublimation although an apparently pure sublimate was obtained on a cold finger in 12% yield based on UF_4. For this compound separation was also effected, after sublimation of excess $MgCp_2$, by extraction of the reaction residue with anhydrous benzene[11] under reduced pressure, a yield of 30% being thus obtained.

In the case of reactions with $NbCl_5$, $MoCl_5$, and WCl_6, no excess $MgCp_2$ nor unreacted metal halide was recovered even on strong heating. These reaction mixtures were extracted with chloroform or toluene and gave unidentified metal compounds containing considerable chlorine, which hydrolyzed to give dienes. The product of the reaction of PCl_3 with magnesium cyclopentadienide was extracted with chloroform, after sublimation of excess $MgCp_2$. Aluminum trichloride reacted completely with $MgCp_2$, no trace of $AlCl_3$ or any product being evolved from the reaction mixture on heating to 300°.

Characterization of Compounds.—Most of the π-cyclopentadienyl compounds listed in Table I have been prepared previously

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[2] A. F. Reid and P. C. Wailes, *Australian J. Chem.*, **19**, 309 (1966).

[3] I. E. Newnham and J. A. Watts, *J. Am. Chem. Soc.*, **82**, 2113 (1960).

[4] W. J. Asker and A. W. Wylie, *Australian J. Chem.*, **18**, 959 (1965).

[5] G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry," Vol. 1, 2nd ed, Academic Press, Inc., New York, N. Y., 1963.

[6] A. J. Popov and G. Glockler, *J. Am. Chem. Soc.*, **74**, 1357 (1952).

[7] (a) M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.*, **24**, 387 (1962); (b) M. D. Taylor, *Chem. Rev.*, **62**, 503 (1962).

[8] W. A. Barber, *Inorg. Syn.*, **6**, 11 (1960).

[9] R. W. G. Wyckoff, "Crystal Structures," Vol. 1, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1963, p 272.

[10] E. O. Fischer and A. Treiber, *Z. Naturforsch.*, **17b**, 276 (1962).

[11] E. O. Fischer and Y. Hristidu, *ibid.*, **17b**, 275 (1962).

TABLE I

REACTIONS OF METAL HALIDES WITH MOLTEN MAGNESIUM CYCLOPENTADIENIDE (ON A 2-G SCALE)

Halide	Moles of $MgCp_2$/mole of halide	Reaction temp, °C	Reaction time, hr	Product	Yield,[a] %
CeF_3	1.5	220	4	$(C_5H_5)_3Ce$	48
CeF_4	2	220	5	$(C_5H_5)_3Ce$	15
$CoCl_2$	1	220	2	$(C_5H_5)_2Co$	10
$CrCl_3$	1.5	220	5	$(C_5H_5)_2Cr$	22
$FeCl_2$	1	250	2	$(C_5H_5)_2Fe$	8
$FeCl_2$	1.5 (10 g)	260	16	$(C_5H_5)_2Fe$	42
$FeCl_3$	1.5	260	1	$(C_5H_5)_2Fe$	10
$MnCl_2$	1	200	4	$(C_5H_5)_2Mn$	10
$MnCl_2$	1 (10 g) + CO	220	16	$C_5H_5\cdot Mn(CO)_3$	25
$MnCl_2$	1 (10 g) + CO + THF	150	16	$C_5H_5\cdot Mn(CO)_3$	37
MnF_2	1.25	230	4	$(C_5H_5)_2Mn$	28
NdF_3	1	260	0.5	$(C_5H_5)_3Nd$	37
NdF_3	1.5	260	4	$(C_5H_5)_3Nd$	39
$PbCl_2$	1	220	0.5	$(C_5H_5)_2Pb$	52
PbF_2	1	200	0.1	$(C_5H_5)_2Pb$	45
ScF_3	1.5	220	3	$(C_5H_5)_3Sc$	83
SmF_3	1.5	260	6	$(C_5H_5)_3Sm$	55
SmI_2	1.0	220	1	$(C_5H_5)_3Sm$	25
ThF_4	2	200	2	$(C_5H_5)_4Th$	61
$TiCl_3$	1.5	230	3	$(C_5H_5)_2TiCl$	nd
$TiCl_4$	2	80–200	0.5	$(C_5H_5)_2TiCl$	15
UF_4	2	230	0.7	$(C_5H_5)_4U$	30
VCl_3	1.5	220	3	$(C_5H_5)_2V$	32
ZrI_4	2	230	1.5	$(C_5H_5)_2ZrI_2$	72

[a] In most cases only one reaction was performed and yields can probably be improved. nd = not determined.

by methods given in the literature.[12-14] The compounds as produced by the present reaction process were each identified as containing C_5H_5 rings bonded with fivefold axial symmetry to the metal atom by examination of their near-infrared combination spectra as described elsewhere.[15] In a number of cases the presence of a single product was checked by examination of the nmr spectrum of the compound in solution in either deuteriochloroform or in tetrahydrofuran, using a Varian A-60 instrument. In each of these cases the characteristic single peak at 6–7 ppm,[16] due to a π-C_5H_5 ring or more than one equivalent ring, was obtained.

The known compounds were in addition variously identified by their colors, melting points or mixture melting points with other samples, elemental analyses, and correspondence of X-ray powder photographs with those of the same compound prepared by other published methods. This last procedure is particularly convenient for identifying members of a series of organometallic compounds such as these, since their powder patterns are quite distinctive and allow easy visual comparison of the patterns obtained from comparison samples. In addition, by this means the tetrakis(cyclopentadienyls) of thorium and uranium were found to be isomorphous.

X-Ray Powder Photographs.—Samples were finely ground in the drybox and loaded into 0.5-mm Lindemann glass capillaries, which were subsequently sealed off without exposure of the contents to air. Photographs were taken on a 114.6-mm powder camera using Cu Kα radiation filtered by nickel.

Melting Points.—Melting points were obtained using samples sealed in capillaries under nitrogen or argon.

Elemental Analyses.—These were performed by the Australian Microanalytical Laboratories, University of Melbourne, and by Mr. E. S. Pilkington of the Division of Mineral Chemistry, CSIRO.

Samples were compacted into pellets in the drybox and transferred under argon. The derivatives of lead, neodymium, thorium, titanium, and zirconium gave carbon analyses within 0.1 to 0.9%, hydrogen analyses within 0.1 to 0.2%, and metal analyses within 0.4 to 1.4% of those theoretically required.

After the separation procedures described above, each of the compounds was tested for magnesium content. In no case could magnesium be detected in the hydrolyzed solutions of the compounds.

Results and Discussion

For preparing the cyclopentadienyl compounds of scandium and the rare earths, the use of the fluorides, which do not react in solution preparations, is particularly convenient as they are often more readily prepared anhydrous than chlorides or other halides.[5,7b] For example, they can be precipitated from alcoholic solutions of the hydrated nitrates,[6] which are in turn made by the action of nitric acid on the oxides. The precipitated fluorides of uranium and thorium are readily dehydrated by heating in a stream of hydrogen fluoride and are relatively stable to atmospheric moisture. Their reaction with magnesium cyclopentadienide in sealed glass tubes is a considerably simpler operation than the solution procedures of Fischer, *et al.*,[10,11] and gives higher yields.

The cyclopentadienyl compounds of thorium, uranium, scandium, and the rare earths all sublime above 180–200°, and their separation from reaction mixtures is particularly simple. Excess $MgCp_2$ is sublimed off at 80–120°, and the product is sublimed from the reaction residue at the higher temperature. This procedure is also satisfactory for the separation of bis(cyclopentadienyl)titanium(III) chloride and bis(cyclopentadienyl)zirconium(IV) iodide. Bis(cyclopentadienyl)lead and bis(cyclopentadienyl)tin can be separated from the more volatile $MgCp_2$ by sublimation along a heated tube. However, separation by physical means of the bis(cyclopentadienyl) derivatives of the

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[12] G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959).

[13] E. O. Fischer, *Advan. Inorg. Chem. Radiochem.*, **1**, 61 (1959).

[14] J. Birmingham, *Advan. Organometal. Chem.*, **2**, 365 (1964), and references there cited.

[15] A. F. Reid, D. E. Scaife, and P. C. Wailes, *Spectrochim. Acta*, **20**, 1257 (1964).

[16] A. F. Reid and P. C. Wailes, *J. Organometal. Chem.*, **2**, 329 (1964).

first-row transition metals from $MgCp_2$ is practically impossible because of their close similarities in melting points and vapor pressures, and, furthermore, in most cases only a moderate or low conversion of the transition metal dihalide was obtained. Chemical separation by removal of $MgCp_2$ with carbon dioxide[17] or chlorinated solvents[2] is useful only for ferrocene. The bis(cyclopentadienyl) compounds of the first transition metal series are better prepared by addition of solvent to the mixture of $MgCp_2$ and metal halide,[2] the latter reactant being in slight excess to ensure complete removal of the magnesium compound from the reaction mixture.

When a cyclopentadienyl metal carbonyl compound is required as the end product, the unseparated reaction mixture can be heated under a pressure of carbon monoxide, or, more conveniently, the metal halide and $MgCp_2$ can be placed together in the pressure vessel and heated together under carbon monoxide. This latter procedure allowed the preparation of cyclopentadienylmanganese tricarbonyl from manganese dichloride. This product was also obtained by heating manganese dichloride, $MgCp_2$, and tetrahydrofuran under carbon monoxide at 150° rather than 220° in the absence of solvent.

It was observed in the reactions of $CrCl_3$, VCl_3, $FeCl_3$, $TiCl_4$, and CeF_4 with excess $MgCp_2$ that reduction of the halides occurred, so that the reaction products were the bis(cyclopentadienyls) of chromium, vanadium, and iron, bis(cyclopentadienyl)titanium(III) chloride, and cerium tris(cyclopentadienide), respectively. Bis(cyclopentadienyl)titanium(III) chloride has previously been shown to be the product of the reaction of $TiCl_4$ with excess $MgCp_2$ in solution,[18] even at elevated temperatures, although sodium cyclopentadienide in solution at 125° gave tris(cyclopentadienyl)titanium.[19] Extraction in a Soxhlet apparatus of solid $MgCp_2$ with $TiCl_4$ was found to give moderate yields of bis(cyclopentadienyl)titanium(IV) chloride, but direct mixing of the reactants caused violent though not immediate reaction. With the use of inert solvent, yields of 75% are obtainable.[20]

Although ThF_4 and UF_4 reacted to give $ThCp_4$ and UCp_4, ZrI_4 gave only bis(cyclopentadienyl) diiodide even with excess $MgCp_2$. Similarly ThI_4 gave an iodine-containing product which appeared to be $(C_5H_5)_2ThI_2$.

Some halides did not react as readily as might be expected, in particular, ZrF_4, $ZrCl_4$, and $ZrBr_4$. Attempts to extend the reaction to metal derivatives other than halides were also unsuccessful, even though the estimated free energies of reaction favored reaction. Among potential reactants which were tried were $FeSO_4$, $MnSO_4$, $K_3Fe(CN)_6$, K_2ZrF_6, $Ni(CN)_2$, ThC_2, and the halides AgCl, CuCl, and $CuCl_2$. In each of these cases the magnesium compound was recovered unchanged after 1–2 hr at 200–250°.

The penta- and hexachlorides $NbCl_5$, $TaCl_5$, $MoCl_5$, and WCl_6 reacted violently when heated with magnesium cyclopentadienide, possibly undergoing reduction, to give black reaction mixtures containing colored metal compounds. These were extractable in chloroform, contained hydrolyzable organic groups and chlorine, and were very reactive toward air. π-Cyclopentadienyl groups were definitely absent, but the infrared spectra indicated the presence of diene-containing ligands. Identification of these products is currently in progress. Both $AlCl_3$ and PCl_3 reacted completely to give nonvolatile compounds. The phosphorus compound could be extracted with chloroform but was rapidly attacked by air, giving an odor of phosphines.

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(17) G. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, **2**, 95 (1956).

(18) A. F. Reid and P. C. Wailes, *Australian J. Chem.*, **18**, 9 (1965).

(19) E. O. Fischer and A. Löchner, *Z. Naturforsch.*, **15b**, 266 (1960).

(20) (a) C. L. Sloan and W. A. Barber, *J. Am. Chem. Soc.*, **81**, 1364 (1959); (b) W. A. Barber, private communication.