remains constant, the reaction is clearly intramolecular. If the carbanion intermediate abstracts a proton from another olefin, H^3 will appear in the untagged olefin. Finally, if the intermediate abstracts a proton from the solvent there will be a decrease in the total activity of the tagged olefin.

The present study was carried out by isomerizing a 0.7 molar solution of a 50–50 weight mixture of pentene-1 and hexene-1 in a 0.9 molar solution of sublimed potassium *tert*-butoxide in dimethyl sulfoxide. The pentene reagent contained 0.01 mc./mM. of tritium. Analysis of the pentene as received from The New England Nuclear Corporation showed that it contained about 3% of pentene-2 and that his 3% contained 99% of the tritium. The pentene was tritiated by contacting pentene-1 with sulfuric acid-H^3. Analyses of reactants and products were obtained on a radio-assaying gas chromatograph of the type described by Wolfgang.[5] This system can count tritium at essentially 100% efficiency.

It was found that the 1-olefins were converted completely in 24 hours but there was no measurable H^3 in the isomerized hexenes after 312 hours. (If 1% of the initial H^3 were in the hexenes, it would have been detected easily). At the end of this 312 hour period, the pentenes and hexenes were at thermodynamic equilibrium and the H^3 was equally distributed among the three pentene isomers. There was a gradual decrease in the total H^3 content of the pentenes and at the conclusion of the experiment, the activity had fallen to 65% of its initial value. Thus, the conclusion is reached that the intermediate is exchanging protons with the solvent. Analysis of the dimethyl sulfoxide on the radio-assaying gas chromatograph showed that the solvent contained essentially all of the tritium that had been lost from the pentene.

ISOMERIZATION OF LABELED OLEFIN

7.0 cc. of dimethylsulfoxide; 0.7 g. of KOC_4H_9, 0.38 g. of olefin mixture.

Hours	Feed	1	4	24	48	144	312
Composition, wt. %							
Pentene	47.5	8.7	4.3	1.3	1.8	1.3	1.5
Pentene-2-*t*	1.0	4.1	11.3	20.7	28.1	37.6	33.7
Pentene-2-*c*	0.6	40.1	34.6	21.0	18.0	10.9	9.0
Hexene-1	50.9	7.0	3.3	2.5	1.4	0.8	0.9
Hexene-3	...	...	1.2	9.1	10.6	13.2	14.1
Hexene-2-*t*	...	4.3	6.4	16.0	19.5	24.6	29.5
Hexene-2-*c*	...	35.7	38.9	29.3	20.6	11.7	11.3
Rel. sp. act.[a]							
Pentene-1	2.9	27	50	69	76	72	78
Pentene-2-*t*	3300	972	337	147	117	77	70
Hexene-2-*c*	3300	45	66	55	53	66	74
Total activity	100	105	103	89	82	67	64

[a] Defined as the ratio of the radio peak area divided by the chemical peak area.

In order to obtain a more quantitative estimate of the rate of exchange with the solvent, as compared with the rate of isomerization, it is possible to make a simplified kinetic analysis of the reaction. The values for forward rate constants for reactions (6) and (7) can be obtained at low conversion from

$$\text{Pentene-1} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} cis\text{-Pentene-2} \qquad (6)$$

$$\text{Pentene-1} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} trans\text{-pentene-2} \qquad (7)$$

equations (8), (9) and (10). Since most of the

$$[\text{pentene-1}] = [\text{pentene-1}]_0 e^{-kt} \qquad (8)$$

$$[cis\text{-pentene-2}] = [cis\text{-pentene-2}]_0 + (k_1[\text{pentene-1}]_0/k)(1 - e^{-kt}) \qquad (9)$$

$$[\text{Pentene-2-}t] = [\text{pentene-2-}t]_0 + (k_2[\text{pentene-1}]_0/k)(1 - e^{-kt}) \qquad (10)$$

where: $k = k_1 + k_2$

H^3 is in the pentene-2 isomers the reactions of interest are the reverse of (6) and (7), represented by k_{-1} and k_{-2}. These are obtained by dividing the forward rate constants k_1 and k_2 by the appropriate equilibrium constants. Values for the four rate constants are shown in the table.

k_1	4.8×10^{-4} sec.$^{-1}$	$K_{-1} = 7.83$
k_{-1}	6.1×10^{-1} sec.$^{-5}$	
k_2	3.0×10^{-1} sec.$^{-5}$	$K_{-2} = 25.9$
k_{-2}	1.2×10^{-4} sec.$^{-6}$	

A plot of the log of the total activity remaining *vs.* time shows the decay in radioactivity to be first order and to proceed with a rate constant of 1.2×10^{-6} sec.$^{-1}$. Insufficient information about the detailed mechanism is available to apply an isotope effect but it is clear that exchange with the solvent is occurring at roughly the same rate as isomerization.

The foregoing data lead to the postulation of an intimate complex between base, solvent and reactant olefin. Additional work is presently in progress that should shed more light on the nature of this complex.

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UNUSUAL MAGNETIC PROPERTIES OF SOME SIX-COÖRDINATE COBALT(II) COMPLEXES[1]—ELECTRONIC ISOMERS

Sir:

If attention is restricted to octahedral transition element complexes, for metal ions such as Fe(II), Co(II), etc., an extended series of ligands of increasing ligand field strength would be expected to produce spin-free compounds at the low field extremity and spin-paired compounds at the high field extremity of the series. In the vicinity of that interval within which the pairing energy is comparable to the excess stabilization energy of the spin-paired state, the two spin states are expected to coexist.[2] Here a true electronic isomerism

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[1] Presented at the 136th National Meeting of the American Chemical Society, Atlantic City, New Jersey, 1959.

[2] L. E. Orgel, *J. Chem. Phys.*, **23**, 1819 (1955); Report to the Xth Solvay Council, Brussels, May, 1956.

should be found. Detection and quantitative characterization of the cross-over points between spin states for different metal ions and stereochemistries should provide a stringent test for ligand field concepts in the strong-field realm and offer a basis for extension of the theory. Relevant data are rare. The singlet–triplet equilibrium has been claimed for square planar nickel(II) and these results have been interpreted and applied.[4,5]

A survey[6] of values for the room temperature magnetic moments of cobalt(II) complexes which are probably of coördination number six reveals the occurrence of an essentially smooth variation in moment from about 1.8 to 5.2 Bohr Magnetons. On the basis of the usual considerations, the magnetic moments of six-coördinate cobalt(II) complexes are expected to reside in limited ranges in the proximities of either of the observed extremes.[7–12] In these terms, the remainder of the moments should be viewed as anomalous. We have suggested previously that these anomalous moments arise from an equilibrium between doublet and quartet states.[6,13,14] It is our purpose here to demonstrate the accuracy of this conclusion for a single example, that of bis-(2,6-pyridindialdihydrazone)-cobalt(II) iodide, $[Co(PdAdH)_2]I_2$, a compound having a moment of 3.04 Bohr Magnetons at 300°.[15] The low moment which is exhibited by this complex does not appear to be a solid state effect since the moment is very nearly the same whether determined in solution or in the solid. Analytical data[15] preclude the existence of a significant amount of cobalt(III) complex, while infrared spectral data indicate that the complex is truly six-coördinate.

In order to determine the applicability of the concept of an equilibrium mixture of two spin-states (spin doublet and quartet) the magnetic moment has been determined as a function of temperature over a range of almost 300°. The moment was observed to vary between 1.9 Bohr Magnetons at 80°K. and 3.7 Bohr Magnetons at the high temperature extremity (Table I).

TABLE I

TEMPERATURE DEPENDENCE OF THE MAGNETIC MOMENT OF $[Co(PdAdH)_2]I_2$

T, °K.	μ_{eff}
373	3.69
300	3.04
232	2.49
206	2.33
183	2.20
80	1.90

A very simple treatment leads to gratifying results. By assuming a magnetic moment of 1.9 B.M. for the doublet state and 5.2 B.M. for the quartet state, the mole fraction of each of the two states was calculated for each temperature at which a determination was made (Table II). A plot of log K_{eq} for the reaction

$$\text{Spin-free} \rightleftharpoons \text{Spin-paired}$$

as a function of $1/T$ produces a straight line. The values of $\Delta H°$ and $\Delta S°$ evaluated from this graph are -2.14 kcal./mole and -0.44 e.u., respectively. The significance of $\Delta S°$ is not immediately apparent since alterations are expected in molecular symmetry and bond distances, in addition to the change in electronic degeneracy. From the energy difference between the doublet (lower energy) and quartet states of the complex, and the mean pairing energy of cobalt(II) (64 kcal./mole),[16] the value of Dq would appear to be 2,200 cm.$^{-1}$ (octahedral model), approximately twice that for the tris-(ethylenediamine) complex of cobalt(II).[17]

TABLE II

CONTRIBUTION OF THE SPIN-STATES OF COBALT(II) TO THE OBSERVED MAGNETIC SUSCEPTIBILITY OF $[Co(PdAdH)_2]I_2$

T, °K.	N_1	N_2	K_{eq}
373	0.390	0.610	1.56
300	.218	.782	3.59
232	.084	.916	10.90
206	.054	.946	17.50
183	.030	.970	32.30

Although the wide variation in the value of the magnetic moment leaves no doubt as to the veracity of the over-all interpretation, a number of complications must be mentioned. The treatment given ignores spin–orbit interactions although the magnitude of the constant λ appears to require its inclusion in the reduction of the data.[11] Further, the maximal value of the orbital contribution to the magnetic moment would not appear justified with a ligand of the high donor strength exhibited by PdAdH. These arguments notwithstanding, the best analytical description of the data so far attained is the simple one given above. In contrast, the most rational treatment, that including appropriate spin–orbit corrections for the variation with temperature of the moment assigned to the quartet state produces curvature in the graph of log K_{eq} *vs.* $1/T$.

The fortuitous better agreement of the simple model with the experimental results probably reflects complications not anticipated in the somewhat more refined interpretation. This possibility is supported by the very large value for the ligand field splitting parameter deduced in the first calculation (Dq = 2,200 cm.$^{-1}$). Spectral results obtained on a variety of similar nickel(II) complexes

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(16) J. S. Griffith, *J. Inorg. Nucl. Chem.*, **2**, 229 (1956).

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indicate that ligands such as PdAdH normally exhibit *Dq* values between 1200 and 1400 cm.$^{-1}$ when in combination with divalent metal ions.[18] In the cobalt(II) case, the intervention of a strong non-cubic component may render invalid the calculation of the crystal field stabilization energy in terms of an octahedral model for the spin-paired (doublet) state.

(18) M. A. Robinson and D. H. Busch, unpublished results.

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A NEW ORGANOTIN-MAGNESIUM COMPOUND

Sir:

Organomagnesium compounds of group IV elements ($R_3M^{IV}MgX$) have thus far been reported for the element carbon. Gilman(1) and Seyferth(2) have reported negative results in attempts to synthesize an organomagnesium derivative of germanium. Silyl Grignard reagents, with silicon directly bonded to magnesium, have been postulated by other investigators(3); however, no such reagents have been isolated.

As part of a program on the preparation of organometallics of group III, IV and V elements, we wish to report the preparation and some reactions of a novel organotin-magnesium compound. From its synthesis and reaction products the structure of this compound appears to be $[(C_6H_5)_3Sn]_2Mg$. It can be prepared at room temperature in tetrahydrofuran (THF) solvent by the reaction of triphenyltin chloride with excess magnesium turnings.

$$2(C_6H_5)_3SnCl + 2Mg \xrightarrow[C_2H_5Br]{THF} [(C_6H_5)_3Sn]_2Mg + MgCl_2 \quad (1)$$

The reaction was initiated by ethyl bromide. Without an initiator, no reaction was observed. No reaction took place when diethyl ether was substituted for tetrahydrofuran as solvent.

It appears that a two step process takes place. After the reaction has started, a white precipitate(4) is formed. Color Test I(5) is negative at this stage. With further stirring at room temperature, the white precipitate disappears and the reaction mixture turns grayish-green in color, and now gives an intense positive Color Test I.

$$2(C_6H_5)_3SnCl + Mg \xrightarrow[C_2H_5Br]{THF} (C_6H_5)_3SnSn(C_6H_5)_3 + MgCl_2 \quad (2)$$

$$(C_6H_5)_3SnSn(C_6H_5)_3 + Mg \xrightarrow[C_2H_5Br]{THF} [(C_6H_5)_3Sn]_2Mg \quad (3)$$

If the mixture was hydrolyzed shortly after the white precipitate is formed but prior to a positive Color Test I, the products identified were $(C_6H_5)_3SnSn(C_6H_5)_3$ and unreacted $(C_6H_5)_3SnCl$. To further substantiate the mode by which this organotin-magnesium compound is formed, hexaphenylditin was allowed to react with excess magnesium in tetrahydrofuran using ethyl bromide as the initiator. The white appearance(4) of the reaction mixture soon disappears with the formation of a grayish-green color, and a positive Color Test I. Hydrolysis of this solution with ammonium chloride solution yields triphenyltin hydride in 82% yield.

$$[(C_6H_5)_3Sn]_2Mg + 2H_2O \longrightarrow 2(C_6H_5)_3SnH + Mg(OH)_2 \quad (4)$$

Carbonation of this organometallic yielded hexaphenylditin as the product. A similar reaction takes place when triphenyltinlithium(6) is treated with carbon dioxide to yield only hexaphenylditin in 80–90% yield.

All the preparations of $[(C_6H_5)_3Sn]_2Mg$ described thus far have been carried out at room temperature. If, however, during the preparation the reaction is refluxed, the organotin-magnesium compound decomposes and hydrolysis yields no triphenyltin hydride.

Other reactions of this organotin-magnesium compound as well as the generality of this preparative method for other elements are currently under investigation.

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(7) University of Dayton, Research Institute, Dayton, Ohio.