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T60*− with Coordination Compounds. (Tetraphen ylporphinato) chromium (III) Fulleride

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Table I. Yields of Products of Reactions of Magnesium with Bromocyclopropane and 1-Bromohexane, Separately and Together, in Diethyl Ether, under Nitrogen, and at Reflux ($\approx$34 °C)[a]

HxBr	CpBr	CpH	CpMgBr	HxMgBr	SS	CpHx	HxS	ΣCp	ΣHx
1		0	0	82	0	0	0		98
	1	40	51	0	7.5	0	0	98	
2	1	40	51	68	7.0	0	0	98	99
1	2	29	64	68	2.2	2.0	6.0	99	99
1	1	28	58	39	1.0	6.6	6.6	95	95
1, 2	2	17	74	58	<1	4.2	5.2	97	97

[a] "1" denotes that RBr was present initially and "2" that it was added, after completion of the initial reaction, for reaction with excess Mg (99.99%, Alfa). Yields are mol of product per 100 mol of CpBr consumed, except that HxMgBr is based similarly on HxBr. The initial concentration of each halide at each reaction stage was 0.18–0.20 M. Mass balances (last two columns) are based on all of the products determined, including HxH, Hx(–H), CpS, and HxHx. Analyses were by titration and gas chromatography, augmented by spectroscopic methods and independent syntheses of unknown compounds, as described in detail elsewhere.[2]

Scheme I
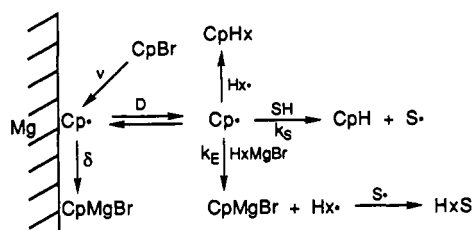
Although there appear to be no previous reports of the occurrence of reaction 2 during Grignard reagent formation, Lawler and co-workers detected it (through CIDNP) in iron-promoted reactions of Grignard reagents with alkyl halides.[10] Kharasch and Fuchs had suggested this possibility earlier.[11] In addition, trapping of polarized R• in reaction 2 could account for the appearance of CIDNP in RMgBr during Grignard reagent formation.[12]

Lehr and Lawler estimate the rate constant as $>10^5$ M^{-1} s^{-1} in THF for reaction 2 with R = isobutyl, R' = ethyl, and X = Br.[10b] According to D-model calculations,[13] a rate constant of 10^5 M^{-1} s^{-1} would not be sufficient to make the reaction very significant during the formation of a 1 M solution of a Grignard reagent. A rate constant as large as 10^6 M^{-1} s^{-1}, however, could lead to significant reaction. The rate constant for the reaction of Cp• with SH is probably near 10^6 s^{-1}.[2,14] The present data indicate that reaction 2 (R = Cp, R' = Hx) is competitive with solvent attack by Cp• when [HxMgBr] $\approx$ 0.2 M. so the rate constant for reaction 2 probably approaches 10^7 M^{-1} s^{-1}. Rate constants for related reactions of alkylborons, -aluminums, -mercuries, etc. can have similar values.[15]

Historically, entrainment has been most often used with aryl halides.[7] Cyclopropyl and aryl radicals, which are σ radicals, are more electronegative than typical alkyl (π) radicals. Since R•/R'MgX exchange can be regarded as a net electron transfer, reaction of σ radicals with alkylmagnesium halides such as ethyl- and hexylmagnesium halides are expected to be thermodynamically favored. Conversely, the Hx•/CpMgBr exchange reaction is expected to be thermodynamically unfavored and therefore relatively slow. Consistent with this, no effects on the yields of

CpMgBr, CpH, and SS are found when magnesium reacts with HxBr in the presence of CpMgBr, and no CpHx or HxS is formed.

The scope of R•/R'MgX exchange reactions, their mechanistic details, accurate values of their rate constants, the extents of their contributions to entrainment in other examples, solvent, halogen, and other effects on R•/R'MgX exchange, and the possible roles of transition-metal impurities all remain to be established.[16]

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$C_{60}^{\bullet-}$ with Coordination Compounds. (Tetraphenylporphinato)chromium(III) Fulleride

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Recent reports of the reductive electrochemistry of C_{60},[1–4] the isolation of the first fulleride salt,[5] the conductivity and superconductivity of alkali metal doped fullerenes,[6,7] and the lithiation of C_{60}[8] suggest that the anions of the buckminsterfullerenes ("bucky balls") have a very rich chemistry. With the charac-

† On leave from the Laboratoire de Physique des Solides, U.A. 2 CNRS, Université de Paris-Sud, 91405 Orsay, France.
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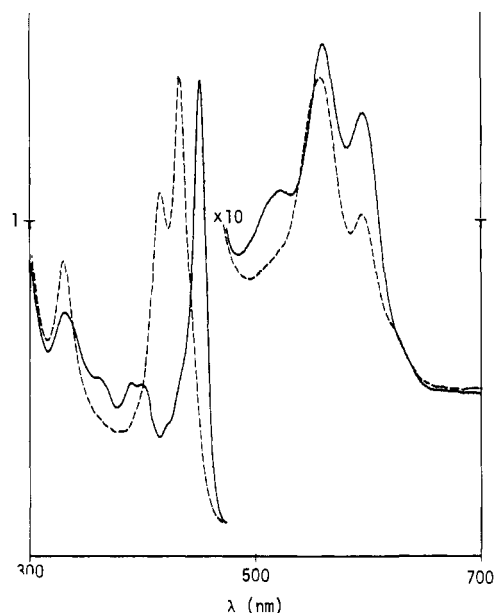
Figure 1. UV–vis spectrum in tetrahydrofuran of the (tetraphenyl-porphinato)chromium(III) C_{60}·⁻ product (solid line) and after air exposure (dashed line) to give C_{60} and a mixture of $Cr^{IV}O(TPP)$ and Cr^{III}_2-(μ-O)(TPP)$_2$.

terization of an η^2-C_{60} platinum complex,[9] the macroscale coordination chemistry of neutral C_{60} is beginning to be explored. We now report the reaction of C_{60} with coordination compounds to give the C_{60}·⁻ anion. The large size, high symmetry, and charge delocalization of C_{60}·⁻ make it a novel candidate for the least-coordinating anion.[10] Its radical nature opens up interesting new possibilities for spin coupling with paramagnetic transition-metal complexes. A salt displaying molecular ferromagnetism has just been reported.[11]

Anaerobic treatment of a crimson solution of $Cr^{II}(TPP)$[12,13] in tetrahydrofuran with a magenta solution of C_{60}[14] in toluene in a 1:1 mole ratio gives a green solution from which purple-black crystals are deposited in nearly quantitative yield. The UV–vis spectrum in THF shows a diminution and shift of the 329-nm band of C_{60} to 331 nm (see Figure 1, solid line). A similar observation in dichloromethane (330 to 339 nm) has been reported for the C_{60} to C_{60}·⁻ electroreduction.[4] A shift in the porphyrin Soret band from 421 to 451 nm is diagnostic of Cr(II) to Cr(III) oxidation.[13] Interestingly, dissolution of the product in toluene completely reverses the redox reaction as judged by the appearance of λ_{max} at 334 nm for C_{60} and 425 nm for $Cr^{II}(TPP)$ in that solvent. Addition of a few drops of THF to the toluene solution promotes the electron transfer again:

$$Cr^{II}(TPP) + C_{60} \underset{toluene}{\overset{THF}{\rightleftharpoons}} Cr^{III}(TPP)^+C_{60}·⁻$$

This critical dependence on solvent is consistent with the lower first reduction potential of C_{60} reported in THF compared to other solvents.[2] It is also consistent with stabilization of the higher oxidation state of chromium by (a) the higher dielectric constant

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(12) Abbreviations used in this paper: TPP = dianion of tetraphenyl-porphyrin; THF = tetrahydrofuran; TPP·⁻ = π-radical anion of TPP.

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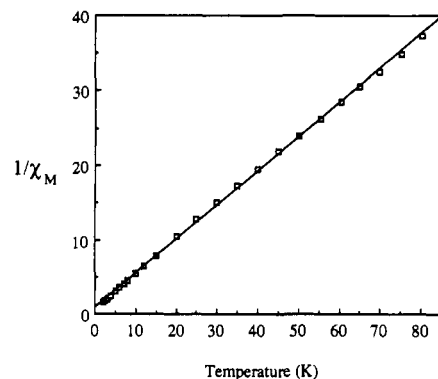
Figure 2. SQUID magnetic susceptibility data at 10 kG. The microcrystalline sample was immobilized in paraffin wax to prevent aerobic oxidation and/or crystal alignment by the applied field. The solid line is a linear regression analysis.

Applied Field →
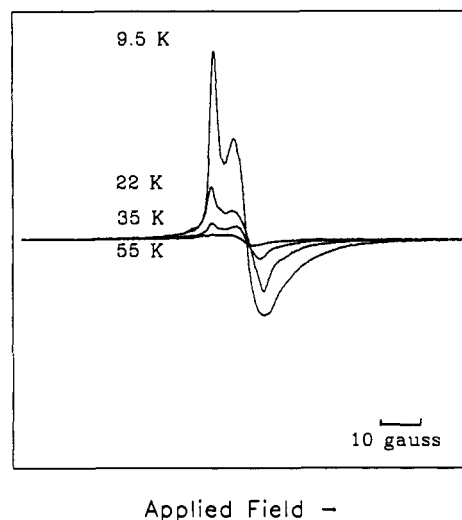
Figure 3. Temperature-dependent X-band EPR spectra in frozen THF solution (10^{-4} M) recorded over a 100-G range with a modulation of 1.25 G.

of the solvent and (b) preferential axial coordination of one or two THF molecules. Chromium(III) porphyrins are known to readily adopt six-coordination[15] whereas chromium(II) porphyrins, although also known with six-coordination, can be isolated as stable four-coordinate species.[13]

In the solid state, elemental analysis indicates a molecular formula of $Cr(TPP)(C_{60})(THF)_3$.[16] The presence of THF solvate molecules does not allow us to distinguish between the two likely structural formulations of an ionic salt, $[Cr^{III}(TPP)-(THF)_2]^+[C_{60}·]^-$·THF, or a coordinated C_{60}·⁻, Cr^{III}-(TPP)(C_{60}·)(THF)·2THF. SQUID magnetic susceptibility measurements (2–80 K, see Figure 2) show essential Curie–Weiss law behavior corresopnding to a room temperature magnetic moment of 4.2 ± 0.1 μ_B. The spin-only value expected of a non-interacting $S = {}^3/_2, {}^1/_2$ system is 4.27 μ_B. The negative Weiss constant ($\theta = -2$ K) is indicative of weak antiferromagnetic coupling, but the data do not distinguish between the molecular field interactions expected from an ionic structure and metal–ligand spin coupling expected from coordination of the C_{60}·⁻ radical to d³ chromium(III). The solid is EPR silent down to 5 K.

In the solution state, EPR and conductivity measurements indicate an ionic formulation. In THF solution, molar conductivities of 24, 26, and 31 ohm⁻¹·cm²·mol⁻¹ are observed for 8 × 10^{-5} (near saturated), 1.6 × 10^{-5}, and 3 × 10^{-6} M solutions, respectively. The values are essentially unchanged by the addition

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of excess 1-methylimidazole, expected to give ionic [Cr(1-MeIm)$_2$(TPP)]$^+$[C$_{60}^{\bullet-}$]$^-$, and are of comparable magnitude to values reported for related 1:1 electrolytes in organic solvents.[15] In saturated frozen THF solution, the temperature-dependent EPR signals shown in Figure 3 are observed. Signals expected for Cr(III) are absent. This is because chromium(III) porphyrin signals extend over ca. 7000 G[15] and detection is limited by solubility. By comparison to previous EPR studies of C$_{60}^{\bullet-}$ which show signals centered at g = 1.999 (2),[2] 2.001,[4] and 1.997,[17] the observed signals centered at g = 1.995 are ascribed to C$_{60}^{\bullet-}$. Since coordination of C$_{60}^{\bullet-}$ to Cr(III) would be expected to lead to an EPR silent, integral-spin species via magnetic coupling, the observed signals indicate an ionic formulation. We are currently investigating the origin of the anisotropy of the observed signal.

The complex is very air sensitive in both solid and solution states. Visible spectral monitoring indicates that the oxidation products are C$_{60}$ (λ_{max} 329 nm) and a mixture of Cr^{IV}O(TPP) and Cr$^{III}_2$(μ-O)(TPP)$_2$ (Soret 432 and 415 nm, respectively).[17] See the dashed line in Figure 1.

Spectral observations indicate that Al^{III}(TPP$^{\bullet-}$) (Soret 450 nm) is another metalloporphyrin complex which reacts with C$_{60}$ to give a related C$_{60}^{\bullet-}$ redox product (Soret 420 nm).

In summary, with Cr(TPP) we have illustrated a productive route to isolable crystalline complexes having C$_{60}^{\bullet-}$ as the counterion. Unable to compete in solution with THF for ligation to [Cr(TPP)]$^+$, C$_{60}^{\bullet-}$ is a novel example of a very weakly coordinating anion. We are currently probing the details of the structural and magnetic interactions and exploring the generality of this synthetic route which opens up the possibility of isolating complexes with coordinated C$_{60}^{\bullet-}$.

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Unavoidable Time-Dependent Ellipticity Changes of Proteins in the Current CD Measurements

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What we report now is believed to be an unusually urgent topic for many investigators who measure circular dichroism (CD) spectra of proteins. We communicate here about unexpected results obtained with J-600 and J-720 of the Jasco J-series CD apparatus, which have been used by many investigators all over the world. A recent innovation of the CD apparatus has made it possible to magnify a slight change of ellipticity. The magnification itself seems not to be difficult. However, since the magnification was done over the full scale range of ellipticity in the measurements with a Jasco CD apparatus older than J-500, the magnification was limited by the capacity of the Y axis of the X-Y recorder. In other words, since it was impossible to magnify some particular part of ellipticity, for example, from 100 mdeg to 102 mdeg, we might have overlooked a slight, but significant, change.

It was found that the ellipticity of a protein decreases with an increase in measurement time. All of the present data were
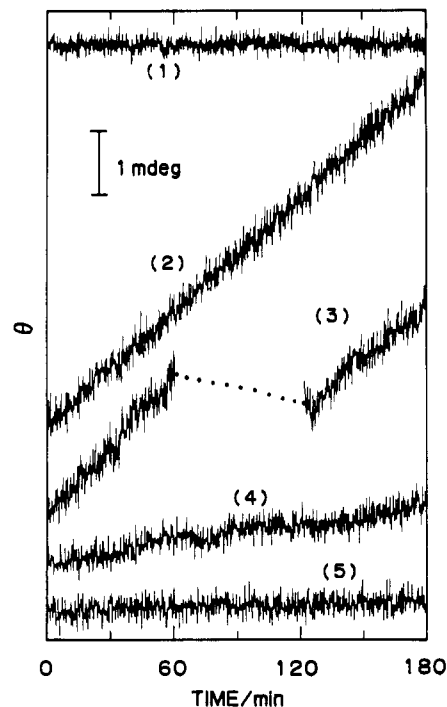
Figure 1. Time-dependent ellipticity changes of pantolactone and proteins at 25 °C: (1) ellipticity (θ) of 0.10% pantolactone at 219 nm, $\theta_{t=0}$ = -125.5 mdeg; (2) and (3) θ of 1.2 × 10^{-5} M BSA at 222 nm, $\theta_{t=0}$ = -140.5 mdeg. In the case of (3), the irradiation was cut off for 1 h; (4) θ of 1.0 × 10^{-5} M myoglobin at 222 nm, $\theta_{t=0}$ = -38.0 mdeg and (5) θ of 6.8 × 10^{-6} M ribonuclease A at 210 nm, $\theta_{t=0}$ = -7.5 mdeg. An upward change corresponds to a decrease of negative ellipticity. The light path length of the cell was 1 mm.

obtained by using CD cell thermostatted at 25 °C with a LAUDA RM6 and by running the apparatus in a room thermostatted at 23 ± 1 °C. Figure 1 shows a time-dependent ellipticity change of bovine serum albumin (BSA), myoglobin, and ribonuclease A together with the stability of the apparatus checked with pantolactone. The stability, checked with an ellipticity drift of pantolactone, was less than 0.2% of its total strength. However, the negative ellipticities of proteins decreased with time. The decrease continued for 11 h, the longest running time in the present work. The decrease at 222 nm was approximately 1.8 mdeg/h (1.3% of its initial strength/h) for BSA. A positive ellipticity of BSA at 192 nm also decreased with measurement time. Time dependence of ellipticity decrease was distinctly observed also for myoglobin (2.3% of its initial strength/h), while it was slight for ribonuclease A. These are results obtained with J-600 (band width, 1.0 nm). The same phenomena were observed with J-720. The ellipticity decrease of BSA at 222 nm was 1% of its initial strength/h with J-720 (band width, 0.5 nm). Figure 1 also shows the effect by the obstruction of the irradiation to the BSA sample. The irradiation was obstructed by leaving a metal of appropriate size in the light path. The ellipticity of BSA did not change as long as the light was cut off. The ellipticity began again to decrease substantially from the magnitude attained before the obstruction of light path. Since temperature of the sample part was confirmed to be unchanged by measuring it in the same situation as usual CD measurements (the CD cell was thermostatted, as mentioned above), there was no possibility that the proteins suffered thermal denaturation due to a rise in temperature (2-3 °C) of the sample room.

The dependence of ellipticity change on the measurement time might be due to some photoreaction in proteins, to which no attention has been paid so far. In order to examine the nature of the photoreaction, the reaction was prominently caused in a short time, as follows. The sample cell, the temperature of which was controlled at 25 °C by circulating water from the thermostat, was kept at the place which was 10 cm away from the lighting (arc discharge) point of a 450-W xenon lamp (the place where