References and Notes

(1) H. W. H. J. Bodewitz, C. Blomberg, and F. Bickelhaupt, *Tetrahedron Lett.*, 281 (1972); *Tetrahedron*, **29**, 719 (1973); **31**, 1053 (1975).

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(5) The spectra in Figure 2 were obtained in the fourier transform mode using a Bruker WP-60 pulsed NMR spectrometer. Each scan represents a single transformed FID. Spectra were accumulated at 1.7-s intervals using a 10° pulse angle to avoid distortion of the CIDNP intensities.[6] In the absence of $FeCl_2$ the Grignard reagent and alkyl halide undergo less than 10% reaction in 0.5 h, as estimated from the NMR of spectrum of the mixture.

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(11) CIDNP from Grignards is also much more difficult to detect than that from the products of the coupling reaction and is simply not observed in many rapidly reacting samples. In an earlier report,[3b] for example, we pointed out that neither halogen–metal exchange nor, by implication, Grignard enhancement could be detected when the alkyl groups were *n*-butyl and *tert*-butyl. Observations made for a specific pair of reactants should therefore not be considered typical of the whole reaction class.

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On the Origin of CIDNP Observed during the Grignard Formation Reaction

Sir:

In a series of papers[1] we have proposed that the formation of Grignard reagents from alkyl halides and metallic magnesium occurs essentially by the reaction of radicals, R·, with surface bound (subscript "s") magnesium halide $\cdot XMg_s$ under the influence of base (eq 1, 2, 3, 4 and 4′):

$$RX + Mg \rightarrow RX\cdot^- + Mg_s^+ \quad (1)$$

$$RX\cdot^- + Mg_s^+ \rightarrow R\cdot + \cdot XMg_s \quad (2)$$

$$R\cdot + R\cdot \rightarrow \overline{R\cdot\,\cdot R} \rightarrow 2{*}R\cdot \quad (3)$$

$$R\cdot + \cdot XMg_s \xrightarrow{\text{base}} RMgX \quad (4)$$

$${*}R\cdot + \cdot XMg_s \xrightarrow{\text{base}} {*}RMgX \quad (4')$$

The solvent dependence of CIDNP and product yields,[1b,c,e] as well as the observation of CIDNP in RMgX itself,[1a,b] were the major evidence for this scheme. They also made it reasonable and attractive to suggest a common reaction step (eq 4 and 4′) leading to both polarized and nonpolarized Grignard compounds.

Recently Lawler and Livant[2] reported the observation of CIDNP in Grignard compounds during metal–halogen exchange reactions in THF, catalyzed by the addition of 10^{-4} M $FeCl_2 \cdot 4H_2O$, rationalizing their results in the following way:

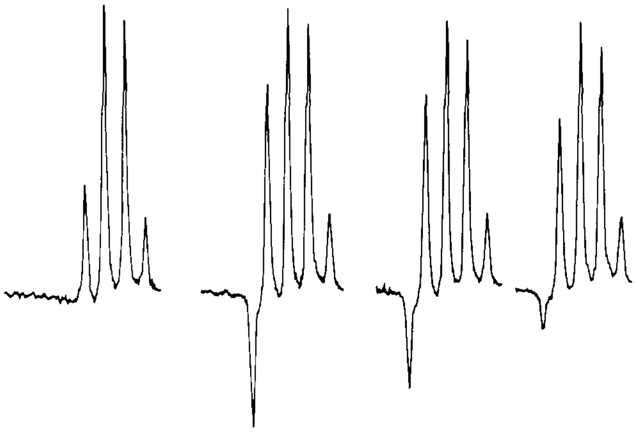

Figure 1. The 60-MHz spectrum in region from 0 to −1 ppm (relative to Me_4Si) before and during the reaction of 0.33 M $(CH_3)_2CHCH_2I$ with magnesium (12 mg) in the presence of 1 M CH_3CH_2MgBr in THF (0.5 ml) at 40°.

$$RX \xrightarrow[\text{catalyst}]{\text{R'MgY and}} R\cdot \quad (5)$$

$$R\cdot + R\cdot \xrightarrow[\text{encounters}]{\text{diffusive}} \underset{1}{\overline{R\cdot\,\cdot R}} \quad (6)$$

$$1 \xrightarrow{\text{combination}} \text{alkanes, alkenes} \quad (7)$$

$$1 \xrightarrow[\text{R'MgY}]{\text{scavenging}} RMgY + R'\cdot \quad (8)$$

They suggested that their results made it likely that CIDNP, observed in our experiments, in the Grignard formation reaction was not due to radicals originating from sequence eq 1–4 but from the reactions given in eq 5–8. This suggestion was based on the idea that small amounts of oxidizing impurities in combination with trace impurities native to magnesium of the grade employed in our laboratory[3] exhibit catalytic activity in the reaction of an alkyl halide with its Grignard reagent, equivalent to added $FeCl_2$.

We wish to present additional evidence which proves that neither are the radicals, responsible for CIDNP in the Grignard formation reaction, formed by process 5, nor do they—to any observable extent—react according to eq 8.

We observed no reaction at all when preformed Grignard reagent is mixed with alkyl halide in diethyl ether or in di-*n*-butyl ether. In THF also no reaction was observed between an alkyl bromide and a Grignard compound. Only on addition of an alkyl iodide (4.5 M) to a Grignard compound in THF (3 M), very weak polarization could be detected in the starting Grignard; polarization in the newly formed Grignard (eq 8) was either absent or too weak to be conclusively observable. With alkyl iodide slow metal–halogen exchange and Wurtz-type coupling were observed.[4] Concentration—varied between 0.5 and 3–4 M in both reactants—was of no influence on these phenomena.

The difficulty to observe the elusive and weak polarization under these conditions[2] is in sharp contrast with the ease with which CIDNP is observed in the Grignard formation reaction. This could be even more dramatically demonstrated by addition of isobutyl iodide (1 M) to a solution of ethylmagnesium bromide (1 M) in THF containing magnesium metal (Figure 1). In contrast to the observation made by Lawler (ref 2, Figure 2) a pure multiplet spectrum (E/A) was observed for the newly formed isobutylmagnesium iodide only, the spectrum of ethylmagnesium bromide remaining unchanged; this implies that ethyl radicals (R′ in eq 8) were not involved in radical pair formation and that combination of polarized radicals, resulting from eq 2 and 3 with ·MgX is the predominant pathway to polarized RMgX. So, contrary to the suggestion made by Lawler and Livant,[2] trace impurities native to our magnesium do not effectuate CIDNP due to reactions 5-8 and therefore are not equivalent to added $FeCl_2$.

Results, similar to those mentioned above, were obtained for other alkyl bromides and iodides and also in di-*n*-butyl ether. The solvent dependence of CIDNP is opposite for uncatalyzed metal-halogen exchange and Grignard formation: in the first case it is observed in strongly basic THF only,[2] in the latter it increases with decreasing solvent basicity.[1c]

A second point which we want to discuss in relation to the sequence 5-8 is the influence of the concentration of preformed Grignard reagent (R′MgY) on the intensity of CIDNP in the newly formed Grignard reagent; both from reaction 5 and reaction 8 (a SH2 type reaction on magnesium) it is to be expected that polarization would increase with increasing concentration of preformed R′MgY. No such increase was observed in a series of experiments in which 0.5 M isobutyl bromide was treated with magnesium in the presence of ethylmagnesium bromide (0, 0.3, 0.7, 1, 1.5, and 2 M) in THF. On the contrary a decrease in the intensity of CIDNP was observed in the newly formed Grignard reagent which can be attributed to both increasing viscosity of the reaction medium as well as the decreasing amount of uncoordinated solvent present.

The results of these experiments exclude SH2 type reactions on magnesium. This is in agreement with the results of an experiment where polarized radicals were created photochemically in the presence of ethylmagnesium bromide;[5] in this case also no SH2 type reaction was observed. Under similar conditions SH2 reactions have been reported for other metal centers.[6] Therefore, the question arises if not processes other than eq 8 are responsible for the incorporation of polarized radicals into the Grignard compound even in the metal-halogen exchange reaction.

However, it might be argued that the SH2 reaction is inefficient under ordinary Wurtz-type reaction conditions but exceptionally efficient under Grignard formation conditions, because in the latter case relatively high concentrations of monosolvated and unpolymerized Grignard species, i.e., RMgX·ether, might be present. It is conceivable that this species would be more susceptible to radical attack both for electronic and especially for steric reasons. Although there are no experimental data to exclude this possibility there is no need for it either, in order to explain the experimental data obtained for the Grignard formation reaction.[1,7]

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(3) All Grignard reagents were prepared from magnesium crystals (Specpure from Johnson and Matthey, Chemicals Ltd., London) with the following impurities: Si 3 ppm, Fe 2 ppm, Cu 1 ppm, Mn 1 ppm, Al, Ca, and Pb <1 ppm.

(4) Except for methyl iodide which gave fast reactions; cf. L. I. Zhakharkin, O. Yu. Okhlobystin, and K. A. Bilevitch, *J. Organomet. Chem.*, **2**, 309 (1964).

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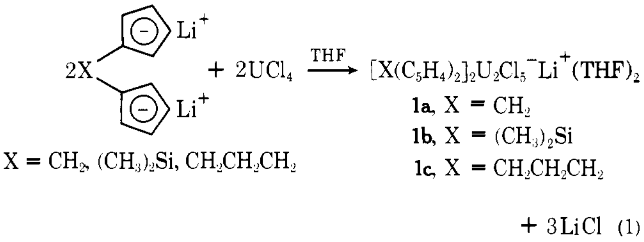
Ring-Bridged Biscyclopentadienyluranium(IV) Halides

Sir:

The pronounced differences in chemical properties of $(\eta^5\text{-}C_5H_5)_3UR$ and UR_4 systems suggest that coordinative saturation is a key factor controlling many reaction patterns of organoactinides.[1] The above two systems represent extremes in this respect, and precursors intermediate in coordinative saturation might be expected to have a far more flexible and elaborate chemistry. The instability with respect to ligand redistribution of plausible[2] starting materials such as $(\eta^5\text{-}C_5H_5)_2UCl_2$[3] has seriously impeded testing of the above hypotheses. We report here an effective synthetic approach to a series of highly stable biscyclopentadienyluranium(IV) halide systems, the unusual molecular structure of one such derivative, and some initial observations on the chemistry.

Anionic biscyclopentadienides[4] containing a variable bridging group react with uranium tetrachloride in tetrahydrofuran (−78°) to yield, after extractive workup (Soxhlet extraction with pentane), dark-red air-sensitive crystalline materials (eq 1).



The new compounds have been characterized by elemental analysis as well as vibrational, ^1H NMR, and mass spectroscopy.[5] Crystals of **1a** were grown from toluene/pentane at −20° and are orthorhombic, space group $P2_12_12_1$-$D_2{}^4$ (No. 19) with $a = 11.510\ (3)$ Å, $b = 15.357\ (4)$ Å, $c = 19.036\ (5)$ Å, and $Z = 4$. Three-dimensional diffraction data were collected on a Syntex $P\bar{1}$ autodiffractometer with slow θ-2θ scans and graphite-monochromated Mo $K\bar{\alpha}$ radiation. The structure was solved using the heavy-atom technique and the resulting structural parameters have been refined to convergence ($R = 0.060$ for 1731 independent reflections having $2\theta_{MoK\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$) in cycles of empirically weighted least-squares refinement which employed anisotropic thermal parameters for all uranium and chlorine atoms and isotropic thermal parameters for all remaining nonhydrogen atoms. Although the combination of very "heavy" atoms, a noncentrosymmetric space group, and crystals with only marginally acceptable diffractive properties prevented a highly precise structure determination, it was possible by optimizing the data collection procedures (slow scan rates and long background counts) with monochromated radiation to obtain data of sufficient quality to allow a qualitative and semiquantitative description of the structure. Efforts are presently underway to grow higher quality crystals.

The solid state structure of **1a** consists of discrete, neutrally charged trinuclear units (Figure 1). Each uranium(IV) is bonded to one terminal chlorine, three bridging chlorines, and