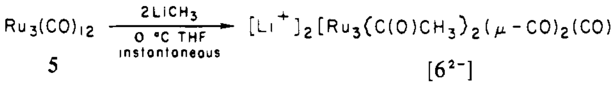
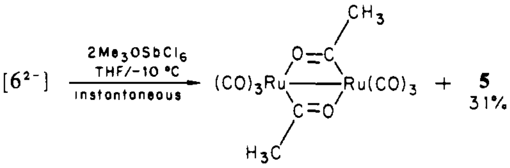


$$Ru_3(CO)_{12} \xrightarrow[\text{0 °C THF, instantaneous}]{2LiCH_3} [Li^+]_2[Ru_3(C(O)CH_3)_2(\mu\text{-}CO)_2(CO)_8{}^{2-}]$$

5 [6^{2-}] (2)



$$[6^{2-}] \xrightarrow[\text{THF/-10 °C, instantaneous}]{2Me_3OSbCl_6} (CO)_3Ru(\mu\text{-}C(CH_3)=O)_2Ru(CO)_3 + 5$$

(3)

5 31%

7, 58%

what the kinetic product may be in the reaction of ethylene with hydrido–triosmium complexes.

(3) Bis(acyl)diruthenium complexes do *not* isomerize.[13] The *kinetic* product of each chemical path in which they are formed is thus *frozen*. The *gem*-bis(acyl)diruthenium complex isolated earlier in the reaction of ethylene with hydrido–acyl–triruthenium complexes can now be identified conclusively as the *kinetic* product.

Acknowledgment. This work was supported by National Science foundation Grant CHE 79-08406.

Supplementary Material Available: Synthetic details and spectroscopic data for $Os_3\{1,2\text{-}\mu\text{-}O{=}CPh\}\{2,1\text{-}\mu\text{-}O{=}CPh\}(CO)_{10}$ (*vic*-**2c**) and $Os_3\{\mu\text{-}Cl,\mu\text{-}O{=}CR\}(CO)_{10}$ (**5**) (R = Me or Ph) (2 pages). Ordering information is given on any current masthead page.

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[13] A possible basis for nontautomerism of the bis(acyl)diruthenium complexes may derive from the short Ru–Ru distance of 2.686 (1) Å as determined for the geminal derivative: Kampe, C. E.; Boag, N. M.; Kaesz, H. D. *J. Mol. Catal.* **1983**, *21*, 297–312. This separation is significantly shorter than Ru–Ru separations in trimeric complexes for which we may take $Ru_3\{\mu\text{-}H,\mu\text{-}O{=}CNMe_2\}(CO)_{10}$ as an example: Szostak, R.; Strouse, C. E.; Kaesz, H. D. *J. Organomet. Chem.* **1980**, *191*, 243–248. In this trimeric complex, the Ru–Ru separations are bridged, 2.8755 (15) Å and unbridged, 2.8319 (15) and 2.8577 (15) Å. Factors operating to shorten the bond in the bis(acyl)diruthenium complexes may lock the acyl groups into the σ,σ-bonded form.

Ab Initio SCF-MO Study of (α-Lithiomethylene)phosphorane

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Received July 25, 1983

In a recent communication, Corey and Kang[2] announced the synthesis and chemistry of (α-lithiomethylene)triphenylphosphorane, which was shown to react as an ylide equivalent in good yield with epoxides and hindered ketones, compounds that are inert to normal Wittig conditions.[3] While alternative methods for increasing ylide reactivity are being explored,[4] α-lithiation promises to become an important means of activating alkylidene ylides, thereby greatly extending their synthetic utility. We report here ab initio SCF-MO studies of (α-lithiomethylene)phosphorane, a prototypical lithiated ylide, and its corresponding free anion.

The geometries of (α-lithiomethylene)phosphorane and the methinylphosphoranyl anion were optimized at the 3-21G+(*)[5] level, by the gradient technique available in a modified version[6] of GAUSSIAN80.[7] Although no symmetry was assumed in the optimizations, both species had global minima possessing C_s symmetry. The results are shown in Table I.

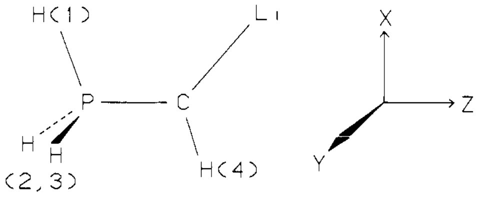
Table I. 3-21G+(*) Optimized Geometries of H_3PCHLi and H_3PCH^-

	H_3-PCHLi	H_3-PCH^-		H_3-PCHLi	H_3-PCH^-
Bond Lengths, Å			Bond Angles, Deg		
P-C	1.67	1.64	H(4)-C-P	114.0	119.9
P-H(1)	1.40	1.40	Li-C-P	131.2	
P-H(2,3)	1.42	1.46	H(1)-P-C	112.9	111.3
C-H(4)	1.09	1.09	H(2)-P-H(3)	95.4	91.3
C-Li	1.92		H(2)-P-H(3)[a]	34.0	28.6

[a] Dihedral angle, with *YZ* plane.

Integrated spatial electron population analysis was used to determine the charge distributions in the two systems.[8] Division of a molecule into fragments demarked by saddle points in the projected electron-density surface yields, upon integration, the spatial electron populations of the fragments.[9] Such populations provide quantitative measures of the effective charges on reactive sites in a molecule. Using the optimized geometries in Table I, we calculated SCF wave functions at the 3-21G+*[5] level for both compounds, and the resulting electron-density surfaces were partitioned as described above. The lithiated ylide has a lithium population of 2.20 electrons and a –CH fragment population of 8.78 electrons. By comparison, the –CH fragment population of the free anion is 8.82 electrons and corresponds essentially to a methinyl dianion bonded to a phosphonium cation. That is, the lithiated species shows a large degree of charge transfer from lithium to carbon and the reactive methinyl group bears essentially the same charge in the lithiated ylide as in the anion. This simple ion pair picture is also supported by the striking similarity in the geometries of the lithiated ylide and its free anion that suggests a cation located at the electrostatic minimum with respect to interaction with the anion. In common with most organolithium compounds, this species is expected to exist as aggregates in solution.[10] We have found the degrees of charge transfer in methyllithium oligomers to be essentially the same as in the monomeric salt;[11] thus the electronic structures of (α-lithiomethylene)phosphorane aggregates in solution are expected to be closely similar to that of the monomer calculated here.

We conclude that (α-lithiomethylene)phosphorane is best described as a contact ion pair whose chemistry is largely that of the corresponding free anion. α-Lithiation increases the inherent nucleophilicity of the alkylidene ylide, but the concomitant



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0002-7863/84/1506-4047$01.50/0

structural changes also result in increased reactivity with hindered substrates. In the parent ylide, methylenephosphorane, the methylene group lies in a plane that, with respect to the molecular orientation in Table I, forms a dihedral angle of approximately 20° with the Y–Z plane.[12] Deprotonation of the ylide results in a rotation of the remaining methylenic hydrogen to lie in the X–Z plane (Table I). This rotation orients the lone pair electrons of the carbanion in a sterically favorable position for the Dunitz trajectory[13] attack upon the carbonyl system of a hindered ketone. The arrangement of atoms in the carbanion moiety of the parent ylide precludes such an attack.

Acknowledgment. This research was supported in part by Air Force Office of Scientific Research Grant AFOSR 82-0114. The VAX 11/750 used for part of this work was purchased with the help of NSF Equipment Grant CHE-8214313.

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Quantitative CIDNP Evidence for the S_H2 Reaction of Alkyl Radicals with Grignard Reagents. Implication to the Iron-Catalyzed Kharasch Reaction

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Received February 10, 1984

Despite years of study, the iron-catalyzed reaction of an alkyl halide and a Grignard reagent remains unsettled.[1-3] It is generally agreed that the Grignard reagent reacts with Fe(II) or Fe(III) to give an activated form of iron, possibly Fe(I) or Fe(0), by a nonradical pathway.[1] The organic products as a result of the reduction of iron appear to be exclusively disproportionation products of the alkyl iron intermediates, (1) and (2). The reduced form of iron is recycled by electron transfer to alkyl halide producing an alkyl radical and halide ion, (3). Both radical trapping experiments[2] and CIDNP results[3] indicate that free radicals are derived only from alkyl halide. Controversy exists over the importance of radical pair reactions in the product-forming steps. Due to the apparent lack of alkyl dimers, Kochi et al.[1,2] propose that free radicals are trapped by iron to give alkyl iron intermediates identical with those formed by reaction with Grignard reagent, (4). Allen et al.,[3] however, report that at high reagent concentration and rates, significant amounts of dimer are formed, (5). Free radicals have also been reported to react regeneratively with alkyl halide, (6), and with Grignard reagent by S_H2 reaction on Mg effecting halogen–metal exchange,[4] (7) (Scheme I). Reactions 4, 6, and 7 represent competitive reactions first order in free radicals whose relative rates should be dependent on the concentration of Fe, RX, and R′MgX, respectively. We wish to report here on quantitative CIDNP evidence which establishes the minimum rate constant for the S_H2 reaction of isobutyl radical and ethylmagnesium bromide, indicating that (4) is not important at typical catalyst concentrations.

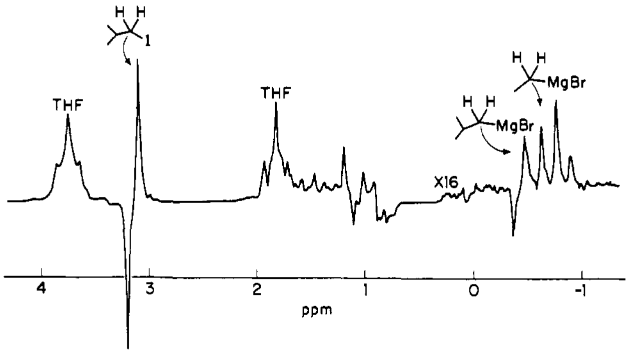

Figure 1. ^1H NMR spectrum (60 MHz) during the reaction of isobutyl iodide and ethylmagnesium bromide catalyzed by 2.0×10^{-5} M Fe(acac)$_3$.

Scheme I

$$R'MgX + Fe_{ox} \xrightarrow{k_1} R'Fe_{ox} + MgX^+ \qquad (1)$$

$$R'Fe_{ox} + RFe_{ox} \xrightarrow{k_2} RH,R'H+ R(-H),R'(-H) + Fe_{red} \qquad (2)$$

$$RX + Fe_{red} \xrightarrow{k_3} R\cdot + X^- + Fe_{ox} \qquad (3)$$

$$R\cdot + Fe_{red} \xrightarrow{k_4} RFe_{ox} \qquad (4)$$

$$R\cdot + R\cdot \xrightarrow{k_5} RH + R(-H) + RR \qquad (5)$$

$$R\cdot + RX \xrightarrow{k_6} RX + R\cdot \qquad (6)$$

$$R\cdot + R'MgX \xrightarrow{k_7} RMgX + R'\cdot \qquad (7)$$

Qualitative CIDNP during the reaction of a primary iodide and primary Grignard exhibits polarization predominantly from halide-derived radicals. The same reaction with a secondary Grignard results in approximately equal magnitude polarization from halide- and Grignard-derived radicals while the reaction with tertiary Grignard results in polarization almost exclusively from Grignard-derived radicals.[5] The reactivity toward Grignard–halide exchange therefore correlates with the radical stability of the alkyl fragment of the Grignard reagent. Product yields for the halide/Grignard pairs methyl/*n*-propyl, ethyl/isopropyl, and ethyl/*tert*-butyl support this conclusion.[2]

Figure 1 shows the CIDNP spectrum obtained during the reaction of 0.8 M isobutyl iodide and 1.6 M ethylmagnesium bromide in THF catalyzed by 2.0×10^{-5} M Fe(acac)$_3$.[6] As reported previously,[4] EA polarization in the α-protons of the newly formed isobutylmagnesium bromide (-0.5 ppm) is consistent with the scavenging of free isobutyl radicals by unreacted Grignard reagent. EA polarization is also apparent in the α-protons of the isobutyl iodide (3.1 ppm), indicating competitive scavenging of isobutyl radicals by unreacted iodide. A small contribution to the polarization in the iodide region due to ethyl iodide as well as an EA dehancement of the signal due to ethylmagnesium bromide indicates that ethyl radicals are present as well.

From a steady-state analysis of the competitive reactions 8–10

$$R^*\cdot + RI \xrightarrow{k_i} R^*I + R\cdot \qquad (8)$$

$$R^*\cdot + R'MgBr \xrightarrow{k_m} R^*MgBr + R'\cdot \qquad (9)$$

$$R^*\cdot \xrightarrow{1/T_{1,R}} R\cdot \qquad (10)$$

(* denotes nonequilibrium nuclear spin population) and the assumption that the polarization intensity is much greater than the equilibrium Boltzmann intensity, the following relationship for the relative polarization intensities of isobutyl iodide and isobutylmagnesium bromide can be derived,[7]

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