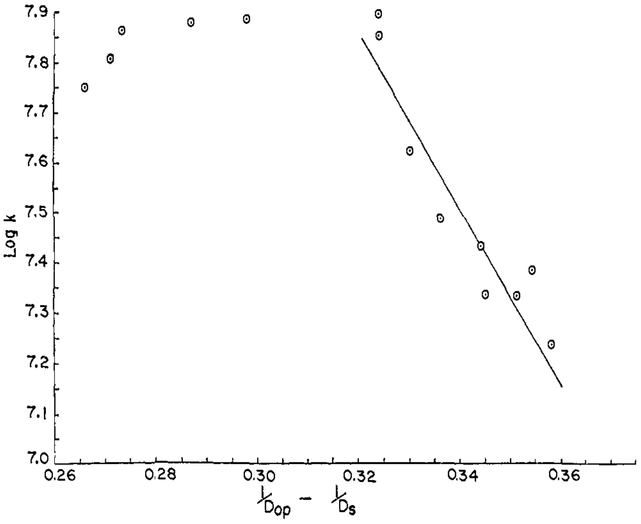

Figure 2. Log *k* *vs.* $(1/D_{op} - 1/D_s)$ for the sodium naphthalenide system at 25°.

Figure 2 is a plot of ln *k* *vs.* $(1/D_{op} - 1/D_s)$ for the sodium naphthalenide system at 25°. The static and optical dielectric constants were measured in the course of this work.[14] In the region of low naphthalene concentration [high values of $(1/D_{op} - 1/D_s)$] Marcus' relation is indeed obeyed. However, at high concentrations the curve deviates significantly from linearity. The reason(s) for this behavior is not certain, but we believe that it may be due to a combination of factors. The most appealing explanation is that we have altered the dielectric constant enough to change the nature of the ion pair. One might argue that at high $C_{10}H_8$ concentrations (lower dielectric constants) a tighter binding of metal to the hydrocarbon is favored, which results in a reduction of the rate constant. In addition, we note that at these high concentrations the esr spectra are collapsed into a single line so that we are no longer certain of the exchanging species involved in the reaction. Over the linear region a value of (1.8 ± 0.3) Å is calculated for *a*.

One might expect that the mechanism of an atom-transfer reaction such as (1) would involve the formation of a sandwich-type complex consisting of a sodium atom between the two naphthalene rings.[15] Assuming the crystallographic radius for the sodium ion (*ca.* 1 Å), we obtain a value of ~1 Å for the "thickness" of a naphthalene ring. This is some 1–1.5 Å less than previous estimates of the thickness of aromatic hydrocarbon ions.[3] Similarly, theoretical calculations[4–6] also predict that the metal–hydrocarbon distance should be in the neighborhood of 3 Å for the splitting (*ca.* 1 G) with which we are dealing. Thus, the size of the activated complex seems to be about 1–1.5 Å less than one would estimate from the data on static ion pairs. However, since we are dealing with an activated complex, it is not unreasonable that it would be somewhat smaller than an unreacting species. Initial measurements on the potassium naphthalenide system indicate that *a* is larger than that for the sodium system. Further experiments are in progress and will be reported at a later date.

Although such an experiment as we have reported here does not measure directly the metal–hydrocarbon distance in an ion pair, it could provide information about the change in the radius of the activated complex with solvent and temperature and thus yield indirect information on the changes in metal–hydrocarbon distances that occur when the metal splitting changes. In view of the lack of experimental data so far, such experiments would clearly be of value. In addition, the experiments are relatively easy to perform and have the advantage that they should be applicable to a large number of systems.

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Extraction of a Phenyl Group from the Tetraphenylboron Anion by Some π-Cyclopentadienyl Derivatives of Ruthenium. A Ruthenium Complex Containing the Tetraphenylboron Anion Directly Bonded to the Metal[1]

Sir:

A previous study of the halogenation of $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ revealed that the bridged halogeno cationic species $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2X]^+$ (X = Cl, Br, and I) are initially formed in these reactions and that nucleophilic attack of halide ions on the latter gives $(\pi\text{-}C_5H_5)Fe(CO)_2X$.[2] It has now been established that the reaction of $\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2$ with iodine in toluene at room temperature in the presence of $NaB(C_6H_5)_4$ and a little methanol parallels the corresponding reaction involving $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ and yields the stable bridged iodo derivative $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2I]B(C_6H_5)_4$. Similarly, the analogous bromination and chlorination reactions afford $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]B(C_6H_5)_4$ (X = Br and Cl). These latter products decompose rapidly in solution, however, and the cations $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]^+$ (X = Br and Cl) were best isolated and characterized as the yellow hexafluorophosphate salts. If the reactions of $\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2$ with bromine and chlorine in toluene in the presence of NH_4PF_6 and methanol are performed at −80°, green products are observed to separate from

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[1] Presented at the 21st Convention of the South African Chemical Institute, Grahamstown, Feb 1–4, 1971.

[2] R. J. Haines and A. L. du Preez, *J. Chem. Soc. A*, 2341 (1970).

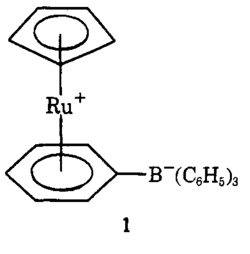
solution. These compounds revert to the yellow species, $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]PF_6$ (X = Br and Cl) at room temperature in both solution and in the solid state and consequently could not be obtained analytically pure. The infrared spectra of these green complexes correspond with those of the yellow $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]PF_6$ (X = Br and Cl) and thus these green compounds are proposed to be a second isomeric form of $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]PF_6$.

The green and yellow isomers of $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]PF_6$ (X = Br and Cl) are very susceptible to nucleophilic attack and react readily with a wide range of anions. For instance, treatment of $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]PF_6$ (X = Br and Cl) in solution with halides and pseudohalides *e.g.*, Cl^-, Br^-, I^-, CN^-, SCN^-, and N_3^-, readily leads to the formation of neutral products according to the scheme

$$[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]^+ + Y^- \longrightarrow (\pi\text{-}C_5H_5)Ru(CO)_2X + (\pi\text{-}C_5H_5)Ru(CO)_2Y$$

The cations $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]^+$ (X = Br and Cl) also react readily with the anion, tetraphenylboron, in solution. Fission of a boron–carbon bond in $B(C_6H_5)_4^-$ and transfer of a phenyl group to a ruthenium atom is effected and the products $(\pi\text{-}C_5H_5)Ru(CO)_2X$ and $(\pi\text{-}C_5H_5)Ru(CO)_2\text{-}\sigma\text{-}C_6H_5$ obtained. The anion $B(C_4H_9)_4^-$ is attacked in an analogous manner. Although mercury salts are known to cleave boron–carbon bonds, reactions involving the transfer of a phenyl group from boron to a transition metal atom are not well documented. Two isolated examples are the slow formation of *trans*-$Pt\{P(C_2H_5)_3\}_2(C_6H_5)_2$ from *cis*-$Pt\{P(C_2H_5)_3\}_2Cl_2$ and $NaB(C_6H_5)_4$ in refluxing tetrahydrofuran[3] and the reaction of $[Pt\{P(CH_3)_2C_6H_5\}_2(CH_3OH)CH_3]^+$ with $NaB(C_6H_5)_4$ in solution to give *trans*-$Pt\{P(CH_3)_2C_6H_5\}_2(C_6H_5)_2$.[4] The cyanide and not a phenyl group is extracted from $B(C_6H_5)_3CN^-$ on reaction with $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]^+$ (X = Br and Cl); $(\pi\text{-}C_5H_5)Ru(CO)_2X$ and $(\pi\text{-}C_5H_5)Ru(CO)_2CN$ are formed as products.

The reaction of $(\pi\text{-}C_5H_5)Ru(CO)_2Cl$ with $NaB(C_6H_5)_4$ in ethanol under reflux is also observed to afford the σ-phenyl derivative $(\pi\text{-}C_5H_5)Ru(CO)_2\text{-}\sigma\text{-}C_6H_5$. The corresponding reaction involving $(\pi\text{-}C_5H_5)Ru\{P(C_6H_5)_3\}_2Cl$ does not afford $(\pi\text{-}C_5H_5)Ru\{P(C_6H_5)_3\}_2\text{-}\sigma\text{-}C_6H_5$, however. A product shown not to contain phosphorus is obtained instead, and this has been characterized as $C_5H_5RuB(C_6H_5)_4$. The presence of four strong bands in the 1500–1350-cm^{-1} region of the infrared spectrum of this derivative is indicative of one of the phenyl rings of the tetraphenylboron being π bonded to the ruthenium atom.[5,6] The sandwich structure shown (1) is thus proposed for this zwitterionic species.[7]



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(7) Although a number of Rh and Ir derivatives containing a tetraphenylboron anion directly bonded to the metal atom through an arene ring have recently been reported,[5,6] compounds with sandwich structures which contain this ligand are not known.

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General Approach to the Synthesis of α-Patchoulane Sesquiterpenes. The Intramolecular Lewis Acid Catalyzed Addition of Diazo Ketones to Olefins

Sir:

The presence of a wide variety of sesquiterpenes which possess the α-patchoulane skeleton **1** in patchouli oil,[1] Indian valarian root oil,[2] and various cyperus oils[3] has been reported, but evaluation of the odor and flavor of many of these sesquiterpenes has been limited due to the lack of synthetic means for attaining working quantities of these compounds. Although specific syntheses of individual α-patchoulane type sesquiterpenes[4–8] have been recorded, it was the objective of our work to develop a general synthetic approach which would be adaptable to all of the sesquiterpenes in this series. We record here such a general, albeit multistep, approach to the α-patchoulane skeleton using as the target compounds the sesquiterpenes *dl*-

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