The analogy between H^+ and $CuL^{+/0}$, L = neutral/−1 ligand, or $AuL^{+/0}$ has been noted and can be useful in cluster chemistry.[19] However, small differences in bond energies can change the nature of products obtained from reaction with H^+ as compared with $CuL^{+/0}$. As seen in eq 2, the reaction of I with H^+ leads to protonation of carbon and the loss of the ketenylidene structure.[2] Compound II may represent an analogue of the intermediate or transition state in the protonation reaction.

Very recently, $[PPN]_2[Ru_3CuI(CO)_9(CCO)]$ was prepared in a manner similar to the synthesis of II.[20] Initial spectroscopic data suggest that copper caps the metal face opposite the ketenylidene ligand to give a tetrahedral $CuRu_3$ framework. Thus, the ruthenium ketenylidene exhibits similar chemistry for both $CuL^{+/0}$ and H^+ since both add to the ruthenium framework.

Acknowledgment. A.S.G. was supported by a research fellowship from the Great Lakes Pew Science Program. Additional support came from the NSF Synthetic Organometallic Chemistry Program. We thank Prof. David Phillips for information on the interaction of Cu(I) phosphine complexes with I.

Supplementary Material Available: Listings of crystal data, positional and thermal parameters, and bond angles and distances (9 pages); listing of observed and calculated structure factors for $[PPN]_2[Fe_2CuI(CO)_9(CCO)]$ (44 pages). Ordering information is given on any current masthead page.

---

(18) Sappa, E.; Tiripicchio, A.; Carty, A. J.; Toogood, G. E. *Prog. Inorg. Chem.* **1987**, *35*, 437.

(19) Evans, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *232*, 171. Salter, I. D. *Adv. Organomet. Chem.* **1989**, *29*, 249.

(20) Anal. Calcd for $Ru_3CuIC_{84}O_{10}H_{62}N_2P_4Cl_2$: Ru, 15.57; Cu, 3.29; C, 51.80; H, 3.21. Found: Ru, 16.31; Cu, 3.25; C, 53.04; H, 3.38.

Interionic Contacts in Complex Ion Pairs Detected by Rotating-Frame Nuclear Overhauser Effects

Thomas C. Pochapsky* and Patricia M. Stone

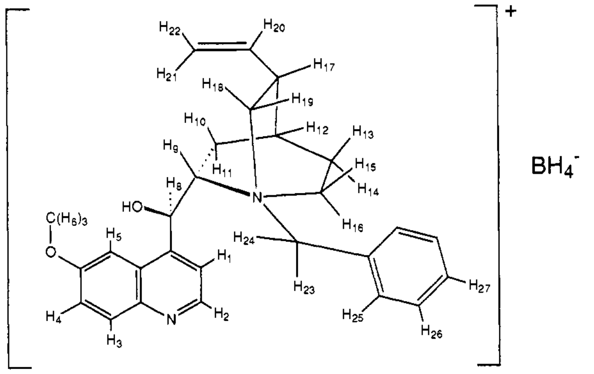
Department of Chemistry, Brandeis University
Waltham, Massachusetts 02254

Susan Sondej Pochapsky

Bruker Instruments, Inc., Manning Park
Billerica, Massachusetts 02181

Received October 18, 1990

The ion pair formed by reagent anion and lipophilic cation are thought to be the reactive species in phase-transfer reactions catalyzed by such cations.[1] As a member of an ion pair, an anion is carried across the phase boundary into nonpolar media in which it may react efficiently with nonpolar substrates. It has been noted that if an asymmetric cation is used as a phase-transfer catalyst, asymmetry is often induced in the products.[2] Information concerning the structure(s) of the ion pair formed in such cases would be valuable in determining the roots of the asymmetric induction and aid in the design of more effective asymmetric catalysts. Recently, we reported the observation of specific $^1H\{^1H\}$ and $^{11}B\{^1H\}$ nuclear Overhauser effects (NOE) to the BH_4^- anion upon selective saturation of the proton resonances of the tetrabutylammonium ion in $CDCl_3$ solution.[3] We have attempted to extend the use of the interionic NOE to determining the structure and dynamics of more complex ion pairs, in particular, that formed by the 8α-9(*R*)-hydroxy-1-(phenylmethyl)cinchonanium ("benzylquininium" or BQ) and the tetrahydroborate ions, **1**, in $CDCl_3$ solution. The BQ ion has been used successfully as an asymmetric catalyst for the phase-transfer reduction of prochiral ketones by BH_4^-,[2] and so ion pair **1** seemed a reasonable point at which to begin these investigations. Unlike the case of the simple ion pair studied previously, however, driven steady-state presaturation NOE experiments on ion pair **1** yielded only a few very weak interionic NOEs which were difficult to interpret. This observation might be rationalized in a number of ways. The ion pair might be solvent-separated, and the lack of observable NOEs due to weak and/or nonspecific association between cation and anion. Alternatively, $\omega_c\tau_c$, the product of the correlation time and the transition frequency being considered, might be close to 1.12, in which case NOEs are not observed regardless of internuclear distance.[4] Generally, for molecules under MW 1000 in nonviscous solvents (short τ_c), this is not a concern. However, aggregation of ion pairs might increase the correlation time sufficiently that the apparent molecular weight of the ion pair is quite large, with concomitant loss of NOE intensity. In this case, interionic NOEs might still be observable when rotating-frame techniques are used (CAMELSPIN[5] or ROESY[6] experiments) in which the observed NOE is always positive and increases monotonically with τ_c.[7] In fact, significant NOEs are observed between the protons of BH_4^- and specific BQ resonances in **1** in the rotating frame.



1

The ^1H spectrum of **1** was completely assigned by using a combination of COSY (*J*-correlated spectroscopy) and ROESY (rotating-frame NOE spectroscopy) data.[8,9,10] Unlike the spectrum of the ion pair studied previously,[3] the ^1H spectrum of **1** shows considerable concentration dependence, especially for the resonances of quinuclidine protons H_9, H_{16}, and H_{18} and the benzyl

---

(1) Weber, W. P.; Gokel, G. W. *Phase Transfer Catalysis in Organic Synthesis*; Springer-Verlag: Berlin, 1977; p 15.

(2) Julia, S.; Ginebreda, A.; Guixer, J.; Masana, J.; Tomas, A.; Colonna, S. *J. Chem. Soc., Perkin Trans. 1* **1981**, 574.

(3) Pochapsky, T. C.; Stone, P. M. *J. Am. Chem. Soc.* **1990**, *112*, 6714–6715.

(4) Noggle, J. H.; Schirmer, R. E. *The Nuclear Overhauser Effect: Chemical Applications*; Academic Press: New York, 1971.

(5) Bothner-By, A. A.; Stephens, R. L.; Lee, J.-M.; Warren, C. D.; Jeanloz, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 811.

(6) Bax, A.; Davis, D. G. *J. Magn. Reson.* **1985**, *63*, 207.

(7) Neuhaus, D.; Williamson, N. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH Publishers Inc.: New York, 1989.

(8) **1** was prepared by exhaustive treatment of a CH_2Cl_2 solution of the chloride salt of BQ, prepared by standard methods, with a concentrated basic aqueous solution of $NaBH_4$. Purity was determined by relative integrations of the BQ and BH_4^- proton signals. NMR samples were prepared immediately prior to spectroscopy in deacidified $CDCl_3$. Samples used for NOE and ROESY experiments were freeze–thaw degassed. Two-dimensional phase-sensitive COSY spectra were obtained on the 500-MHz LDB-500 instrument built by A. Redfield and S. Kunz (Brandeis University). Two-dimensional phase-sensitive ROESY spectra were obtained on a 300-MHz AMX-300 instrument (Bruker Instruments). Data workup was performed by using D. Hare's FELIX program operating on a Silicon Graphics Iris workstation.

(9) For convenience we have used the proton numbering system of Dijkstra et al. for ease of comparison with the spectra of other quinine and quinidine derivatives (Dijkstra, G. D. H.; Kellogg, R. M.; Wynberg, H.; Svendsen, J. S.; Marko, I.; Sharpless, K. B. *J. Am. Chem. Soc.* **1989**, *111*, 8069–8076). Proton resonance assignments for **1** are as follows: (parts per million from TMS, 0.25 M at 25 °C): H_1 7.68; H_2 8.66; H_3 7.92; H_4 7.27; H_5 7.20; H_6 3.90; H_8 6.62; H_9 3.90; H_{10} 1.48; H_{11} 2.21; H_{12} 1.98; H_{13} 1.70; H_{14} 2.26; H_{15} 3.02; H_{16} 4.58; H_{17} 2.51; H_{18} 3.60; H_{19} 3.42; H_{20} 5.61; H_{21} 5.07; H_{22} 4.94; H_{23} 5.51; H_{24} 4.77; H_{25} 7.72; H_{26} 7.33; H_{27} 7.40; BH_4^- 0.30.

(10) Dijkstra, G. D. H.; Kellogg, R. M.; Wynberg, H. *J. Org. Chem.* **1990**, *55*, 6121.

0002-7863/91/1513-1460$02.50/0

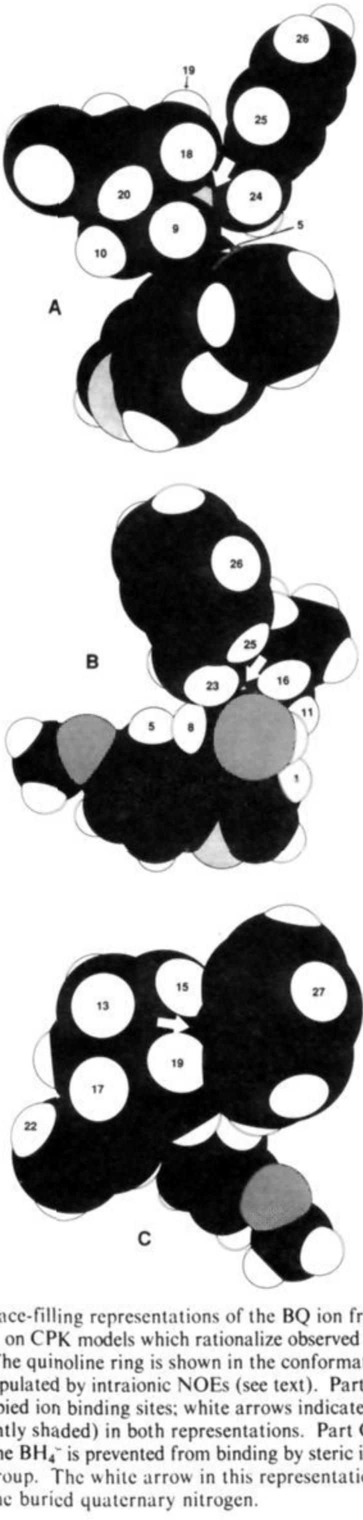


Figure 1. Space-filling representations of the BQ ion from three orientations, based on CPK models which rationalize observed intraionic NOE intensities. The quinoline ring is shown in the conformation determined to be most populated by intraionic NOEs (see text). Parts A and B show the two occupied ion binding sites; white arrows indicate the quaternary nitrogen (lightly shaded) in both representations. Part C shows the site from which the BH_4^- is prevented from binding by steric interactions with the phenyl group. The white arrow in this representation indicates the location of the buried quaternary nitrogen.

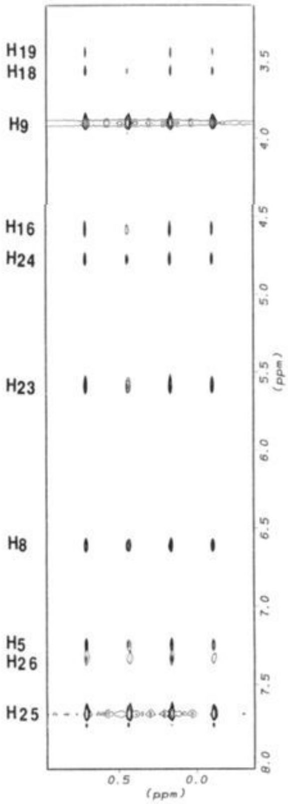


Figure 2. Contour plot of a portion of the 300-MHz ^1H ROESY spectrum of **1** ($CDCl_3$, 0.25 M, 25 °C) showing correlations between the four BH_4^- ^1H lines (corresponding to the four ^{11}B spin states) and ^1H resonances of the BQ ion. Note the series of minor cross peaks at the ω_1 frequencies of H_9 and H_{25} corresponding to BH_4^- containing ^{10}B ($I = 3$, 19.58% natural abundance). A spin-locking period of 250 ms was used, with a spin-lock field of 2.5 kHz ($\pi/2$ pulse = 100 μs).

protons H_{23} and H_{24}. These protons are all in proximity to the phenyl ring, and concentration-dependent chemical shifts may reflect changes in conformational equilibria involving the phenyl group as a result of aggregation. The vinyl group has considerable conformational freedom, with observed NOEs from the vinyl protons H_{20}, H_{21}, and H_{22} indicating that several different rotamers around the C–C bond connecting the vinyl group to the quinuclidine are significantly occupied. Intense NOEs between the quinoline H_5 and protons H_8 and H_9, and between H_1 and H_{11}, as well as very weak NOEs between H_1 and protons H_8 and H_9, indicate that the quinoline ring primarily occupies the rotamer indicated in Figure 1, parts A–C. These representations are based on CPK models which rationalize the observed NOEs. Conformational averaging is observed for proton resonances of both the phenyl and quinoline rings at 300 MHz, 25 °C in the concentration range studied.

Interionic NOEs observed between specific BQ resonances and the BH_4^- protons were used to locate anionic binding sites on the BQ cation. Figure 2 shows a contour plot of the region of the ROESY spectrum containing these NOEs. CPK models of the ion pair indicate that these NOEs cannot result from a single ion binding site, but arise from the approach of the BH_4^- to the cation at two of the four trigonal-pyramidal sites provided by the quaternary nitrogen. Of these four sites, one occurs in the interior of the quinuclidine ring system and is sterically inaccessible to the anion. The two sites that are occupied by the anion a significant percentage of the time, as indicated by the observed NOEs, are shown in Figure 1, parts A and B. Strong interionic NOEs observed between the BH_4^- protons and the ortho phenyl H_{25} and H_9 protons, along with weaker effects at H_{24}, H_{18}, H_{19}, and the quinoline H_5, indicate BH_4^- occupancy of the site shown in Figure 1A. The site shown in Figure 1B is defined by NOEs between the BH_4^- protons and protons H_{25}, H_{23}, H_8, and H_{16}. A weak NOE is also observed to the meta phenyl proton H_{26} from the BH_4^- protons. The third site (Figure 1C) is occluded by the presence of the phenyl ring in space-filling models and is apparently inaccessible to the BH_4^- ion. The absence of NOEs between the BH_4^- protons and H_{15}, which should be seen if this site is occupied by the anion a significant fraction of the time, tend to confirm this. It is not yet clear whether the two sites shown in parts A and B of Figure 1 might be occupied simultaneously as part of an aggregate, or if the sites are only occupied nonsimultaneously, with the observed interionic NOEs resulting from time averaging of different solution structures. We are currently investigating the dependence of the observed NOEs on concentration in an attempt to answer this question.

Acknowledgment. This work was supported in part by a grant from the NIH to Brandeis University (BRSG-S07-RR07044). We are grateful to A. Redfield for his generosity in allowing us to use the LDB-500 NMR instrument, which was built with funds from the NIH (GM-20168).

Arenes with Hafnium(II) Moieties Bonded to Both Faces

F. A. Cotton,* Piotr A. Kibala, and William A. Wojtczak

Laboratory for Molecular Structure and Bonding
Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received October 12, 1990

No molecular compound of Hf(II) not containing a η^5-C_5H_5 group is yet to be found fully described in the literature. Moreover, compounds in which six-membered arene rings are simultaneously and equivalently bonded to two metal atoms lying opposite to each other above and below the center of the ring are rare.[1,2] We report here the preparation of two compounds that embody both of these features. Crystal structures and a molecular orbital formulation of the bonding are also given.

The compounds are $Hf_2I_4(PMe_2Ph)_4(\mu$-η^{12}-arene), where the arene is benzene (**1**) or toluene (**2**). The compounds were synthesized by reduction of HfI_4 with 2 equiv of Na/Hg in the appropriate arene, followed by addition of 2 equiv of dimethylphenylphosphine. The solutions turned immediately red upon addition of the phosphine. The reaction was allowed to proceed for 24 h, at which time the solution was filtered through Celite and layered with approximately 20 mL of hexane. The appearance of red crystalline plates occurred within 3–5 days. The products were obtained in ca. 30% yields and gave satisfactory elemental analysis.

Both compounds have been characterized by X-ray crystallography.[3] Figure 1 shows a molecule of **1** viewed down the Hf–Hf axis and Figure 2 shows a side view of the molecule of **2**. The two molecules are essentially identical in their dimensions. The Hf–I and Hf–P bond lengths have the following ranges and average values: Hf–I, 2.885–2.916, 2.898 (4) Å; Hf–P, 2.780–2.800, 2.787 (4) Å. The C–C bond lengths within the central rings have a range and mean value of 1.41–1.55 and 1.47 Å, respectively. The Hf–C distances are spread over a considerable range, 2.28–2.55 Å, with a mean of 2.42 Å. This is in accord with the small but real ring puckering that can be seen in Figure 2.

The ^{1}H NMR spectrum of **2** shows two signals for the central ring at 3.34 (broad mult) and 3.12 ppm (narrow mult) in an intensity ratio of 3:2. The ^{31}P spectrum of **2** is markedly temperature dependent, suggesting that one or more forms of internal rotation occur. The interpretation of the NMR data is not entirely clear at present, but they seem to imply that while the central ring may be rigidly fixed in the cage of $Hf_2I_4P_4$ atoms at −80 °C, it is rotating rapidly on the ^{1}H NMR time scale at room temperature.

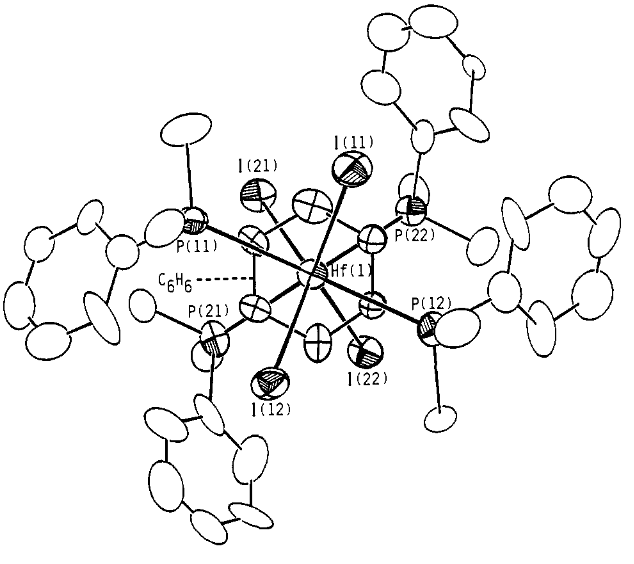


Figure 1. A view of **1** looking down the Hf–Hf axis.

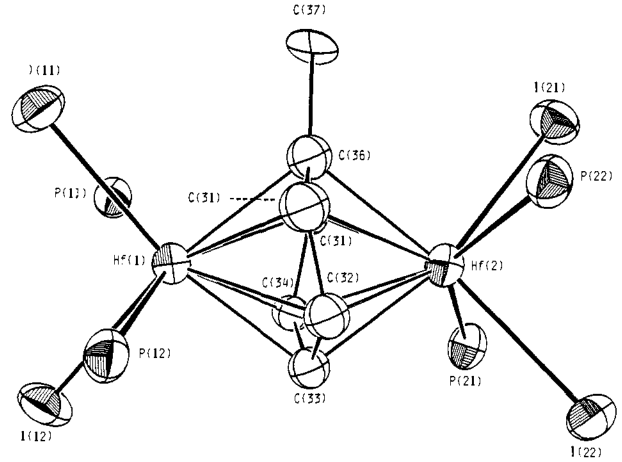


Figure 2. A side view of **2**.

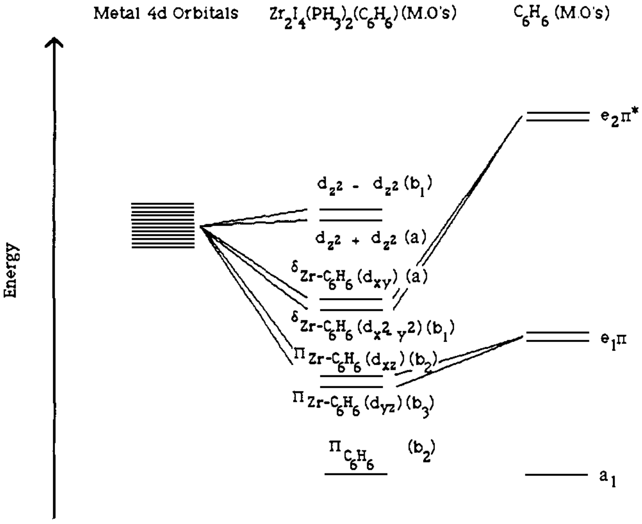


Figure 3. A partial molecular orbital energy level diagram for $Zr_2I_4(PH_3)_2(C_6H_6)$ (D_2 staggered) showing only metal d orbitals and arene π and π^* orbitals.

Finally, we have employed the Fenske–Hall[4] approximation to the Hartree–Fock method to investigate the bonding of the $HfI_2(PMe_2Ph)_2$ moieties to the central benzene ring in **1**. The

---

(1) The first one was reported only in 1983: Duff, A. W.; Jones, K.; Goddard, R.; Kraus, H. J.; Kruger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479.

(2) Lamanna, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 2096.

(3) Compound **1** crystallized in $P2_1/c$ with a = 12.482 (5) Å, b = 13.542 (6) Å, c = 33.857 (15) Å, V = 5722 (7) Å^3, and Z = 4 for an asymmetric unit $Hf_2I_4(PMe_2Ph)_4(C_6H_6)\cdot 2C_6H_6$. With a data/parameter ratio of 7, refinement converged with R = 0.049 and R_w = 0.060. Compound **2** crystallized in $P2_1/c$ with a = 13.612 (6) Å, b = 15.727 (7) Å, c = 22.900 (9) Å, V = 4869 (4) Å^3, and Z = 4 for an asymmetric unit $Hf_2I_4(PMe_2Ph)_4(C_7H_8)$. With a data/parameter ratio of 9, refinement converged with R = 0.049 and R_w = 0.062.

(4) Fenske, R. F.; Hall, M. B. *Inorg. Chem.* **1972**, *11*, 768.

0002-7863/91/1513-1462$02.50/0