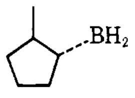
to −25 °C and 5.3 mL of 1-methylcyclopentene (50 mmol) was added. After 2 h at −25 °C, the solution was brought to 0 °C and 10 mL of methanol was added dropwise. Hydrogen, 49.8 mmol, evolved. The solution was treated with 20 mL of 30% aqueous sodium hydroxide, followed by 15 mL of 30% hydrogen peroxide added at such a rate that the temperature was maintained at ~40 °C. After an additional hour at 40 °C, the reaction mixtre was heated under reflux for 12 h to complete hydrolysis of $H_3B{\cdot}NEt_3$. The alcohol products were extracted into ether and dried. Distillation provided 4.0 g of *trans*-2-methylcyclopentanol, bp 72–74 °C (18 mm), 80% yield. The alcohol was then purified by GLC (SE-30 column): $n^{20}{}_D$ 1.4495, $[\alpha]^{27}{}_D$ +24.34°, an optical purity of 55.4%.[3]

Monoisopinocampheylborane, the first optically active monoalkylborane, is evidently an excellent hydroborating agent for hindered (trisubstituted) olefins. It also offers promise for the synthesis of other optically active hydroborating agents, such as **3**, and optically active *trans*-2-methylcyclopentylborane (**4**). Thus, this discovery opens the door to the exploration and development of numerous optically active boranes with considerable potential as hydroborating and reducing agents. It also offers promise of a valuable asymmetric synthesis producing products with defined stereochemistry.



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Necessity of Electron Transfer and a Radical Pair in the Nitration of Reactive Aromatics

Sir:

Aromatic nitration is the canonical example of an established mechanism,[1,2] and it is a model for electrophilic aromatic substitutions and for studies of aromatic reactivity.[2,3] It is the purpose of this paper to demonstrate that the established mechanism is incomplete, and that the "electrophilic" attack on reactive aromatics occurs by electron transfer, followed by radical-pair collapse.

The accepted mechanism of aromatic nitration is

$$H^+ + HNO_3 \overset{\text{fast}}{\rightleftharpoons} H_2ONO_2^+ \longrightarrow H_2O + NO_2^+$$

$$\xrightarrow{\text{ArH}} HArNO_2^+ \xrightarrow{\text{fast}} ArNO_2$$

Frequently formation of NO_2^+ is the rate-limiting step, and electrophilic attack by NO_2^+ on the aromatic is product determining.[1] For aromatics more reactive than toluene, the reaction with NO_2^+ is encounter limited,[4] so that all such aromatics react at the same rate. Yet, even though there is no intermolecular selectivity,[5] there is, paradoxically, intramolecular selectivity. If NO_2^+ is so reactive that it reacts at every encounter with a π system, what distinguishes the ortho and para positions, which have only a slightly greater π-electron density? It is expected that so reactive a species ought to show no selectivity; yet the intramolecular selectivity is ordinary—typical of electrophilic substitutions.[6] The paradox of intramolecular selectivity without intermolecular selectivity is usually interpreted in terms of the intermediacy of π complexes,[7] or oriented encounter pairs:[8]

$$NO_2^+ + ArH \xrightarrow[\text{controlled}]{\text{encounter}} [ArH \rightarrow NO_2^+] \longrightarrow HArNO_2^+$$

It is then asserted[5,7–9] that an oriented π complex can exhibit selectivity. Nevertheless the paradox remains, since it is still necessary to explain how NO_2^+, by virtue of being in a π complex, can acquire selectivity, which free NO_2^+ lacked. Moreover, the estimated lifetime of an encounter pair—10^{-10} s—is too short to accommodate the intramolecular selectivities that are observed. It has been noted[8b] that the intramolecular selectivity in pseudocumene can easily be accommodated if the rate constants for collapse to σ complex at C_6 and C_5 are 10^{11} and 10^{12} s^{-1}, respectively. (According to partial rate factors,[10] which account for the activating effects of methyl groups, C_6 ought to be at least 10 times as reactive as C_2 of toluene; so 10^{11} s^{-1} is a reasonable estimate.) Then both C_1 and C_3 of durene should be considerably more reactive, with rate constants for collapse to σ complex estimated at nearly 10^{13} s^{-1}. Since this is the theoretical maximum, both C_1 and C_3 should react at the same rate. (It has generally been agreed[4] that for sufficiently reactive aromatics the intramolecular selectivity must vanish.) Nevertheless, C_1 of durene is considerably more reactive, since no product resulting from initial attack at C_3 could be detected.[11] Furthermore, the intramolecular selectivity seems to persist even in pentamethylbenzene, which undergoes attack by NO_2^+ predominantly at C_2.[12]

We therefore wish to propose an alternative mechanism—electron transfer, followed by radical-pair collapse to the σ-complex intermediate:

$$NO_2^+ + ArH \xrightarrow[\text{controlled}]{\text{encounter}} \overline{NO_2^{\cdot} + ArH^{+\cdot}} \longrightarrow HArNO_2^+$$

Electron transfer has on occasion been suggested[13] in apparent electrophilic attack on aromatics, and both ESR and CIDNP have been observed.[14] Also, ionization potentials[15] support this suggestion; electron transfer from reactive aromatics to NO_2^+ is exothermic by 20–40 kcal/mol. Of course ionization potentials are gas-phase values, and preferential solvation of NO_2^+ (the smaller ion) decreases this exothermicity. As a result, the electron-transfer mechanism has never been creditable.

To determine the energetics of electron transfer, we have determined the anodic half-wave potentials for NO_2 and representative aromatics in CH_3CN. The experimental values are 1.82 (NO_2), 1.34 (naphthalene), 1.4 (anisole), 1.62 (mesitylene), 1.68 (*o*-xylene), and >1.9 V (toluene) vs. Ag|0.01 M $AgClO_4$. Even in such a polar solvent *electron transfer to* NO_2^+ *is exothermic for all aromatics more reactive than toluene*. Therefore we conclude that the π-complex description is inadequate for a species in which an electron has been transferred from aromatic to NO_2^+.

The electron-transfer mechanism provides a ready explanation for the encounter-limited nitration of aromatics more reactive than toluene. Electron transfer between aromatics and their radical cations is known to be encounter limited whenever the electron transfer is exothermic.[16] Therefore we may expect electron transfer to occur whenever NO_2^+ diffuses to any aromatic more reactive than toluene. Thus we may understand why nitration of *these* aromatics is encounter limited. There is no intermolecular selectivity because all of these aromatics are capable of transferring an electron to NO_2^+ at every encounter.

The electron-transfer mechanism immediately resolves the paradox of intramolecular selectivity without intermolecular selectivity, since NO_2, the attacking species exhibiting the intramolecular selectivity, is different from NO_2^+, the one exhibiting no intermolecular selectivity. In contrast to the electron transfer, radical-pair collapse is quite likely to exhibit selectivity, owing to the nonuniform spin density in the aromatic radical cation. There is a force of attraction between the NO_2 and each carbon of the radical cation (the slope of the bond-dissociation-energy curve). At long distances this force is strongest toward those positions of greatest spin density. At short distances this force is strongest toward those positions where bond formation will produce the most stable σ complex. Thus radical-pair collapse is determined by some composite of spin density and σ-complex stability. This intramolecular selectivity can occur without any activation barrier, and even though electron transfer shows no intermolecular selectivity.

Positional reactivity is better correlated by radical-pair collapse than by electrophilic attack, in those few available cases where they can be distinguished. In nitration of phenanthrene, the order of reactivity is $C_9 > C_1 > C_3 \gg C_2 > C_4$.[17] The relatively high reactivity of C_3 was unexpected and difficult to explain on the basis of Dewar's reactivity index. Likewise, the HMO cation localization energies[18a] suggest a reactivity order $C_9 > C_1 > C_4 \gg C_3 > C_2$, as is observed in protodetritiation.[19] Yet the high reactivity of C_3 in nitration is expected from the HMO spin density, since the coefficients[18b] of the highest occupied MO rank $c_9^2 > c_1^2 > c_3^2 > c_4^2 > c_2^2$. The same sort of agreement is seen in nitration of triphenylene,[20] which produces a 1:1 mixture of 1- and 2-substituted products, as expected from the identity of HMO spin densities,[18c] but quite different from that expected on the basis of cation localization energies[18d] or other electrophilic substitutions.[21]

Similarly, ipso reactivity[22] is better understood in terms of radical-pair collapse. Positional reactivities in the polymethylbenzenes agree fairly well with those estimated[10] according to the additivity principle from the directive effects of the methyl group in toluene. However, the deviations are in the direction expected if spin density becomes increasingly more important in determining the site of attack. For example, C_1 of *o*-xylene, C_4 of *m*-xylene, C_1 of *p*-xylene, and C_1 of durene are positions of high spin density in the radical cations, and show enhanced reactivity.[10,11] Correspondingly, there is diminished reactivity at those positions—C_3 of *o*-xylene, C_2 of *m*-xylene, C_2 of *p*-xylene, and C_3 of durene—where HMO theory predicts low or zero spin density in the radical cation (without the perturbation of C–N bond formation, which permits radical-pair collapse at these positions). Thus the high ipso reactivity in the polymethylbenzenes can be attributed to the spin density at the ipso positions.

An effective test for the existence of an intermediate is to generate it independently and show that it gives the same products, regardless of its origin. We have therefore performed a controlled-potential electrolysis (Pt anode, $E = +1.30$ V vs. $Ag|0.01$ M $AgClO_4$ in CH_3CN) of a mixture of naphthalene and NO_2. According to the half-wave potentials determined above, this applied potential is incapable of oxidizing NO_2, but it suffices to generate the radical cation of naphthalene. Then when the two radicals diffuse together, they can combine to form the σ complex. Indeed, we have found that nitronaphthalenes are produced by this electrochemical synthesis. Moreover, the ratio of 1-nitronaphthalene to 2-nitronaphthalene is 9.2 ± 1, within experimental error equal to the value of 10.9 ± 1 that we have observed in the nitration of naphthalene with HNO_3, H_2SO_4, and urea in CH_3CN. *The observation that the same product mixture is formed both electrochemically and via NO_2^+ is strong evidence that the radical pair is involved not only in the electrochemical synthesis but also in aromatic nitration.*

How general is electron transfer in apparent electrophilic aromatic substitutions? For most electrophiles electron transfer from the aromatic is endothermic. In such cases it is meaningless to invoke a radical pair, even one in equilibrium with π complex; since electron transfer is rapid, this would merely be equivalent to noting that the Born–Oppenheimer approximation is valid during the reaction. Other than NO_2^+, the electrophiles of high electron affinity[15] are H^+, NO^+, and vinyl cations. The electron affinities of H^+ and NO^+ are markedly reduced by solvation, and in their reactions with aromatics the proton-removal step is partially rate limiting. Nevertheless, electron transfer from very reactive aromatics to NO^+ and possibly ArN_2^+ has been observed.[14c,d] Moreover, aromatic substitutions by vinyl cations show normal intramolecular selectivity but low intermolecular selectivity,[23] and it seems likely that these involve radical pairs.

Finally, we note that nitro migrations are unusual in that most electrophiles that rearrange intramolecularly do so by 1,2 shifts,[24] but a nitro group can migrate across a considerable distance.[22a,25] Such a migration is better viewed as a migration of NO_2, via a radical pair, rather than as a migration of NO_2^+, especially in view of the exothermicity of the electron transfer from aromatic to NO_2^+. Indeed, a radical-pair mechanism is well established for the nitramide rearrangement.[26]

In summary, nitration—the classic example of electrophilic aromatic substitution—is not always an electrophilic aromatic substitution, but for reactive aromatics the mechanism involves encounter-limited electron transfer from the aromatic to NO_2^+, followed by radical-pair collapse. This is a necessary conclusion, in view of the exothermicity of the electron transfer and its expected rapidity. As evidence for the involvement of the radical pair, we have shown that electrochemical generation of the naphthalene radical cation in the presence of NO_2 gives the same product mixture as that formed in nitration. Moreover, this mechanism adequately explains the lack of intermolecular selectivity, while intramolecular selectivity and positional reactivity may be interpreted in terms of spin density and σ-complex stability.

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Molecular Structure and Dynamics of $TaCl(\eta^4\text{-}C_{10}H_8)[(CH_3)_2PC_2H_4P(CH_3)_2]_2$

Sir:

Among the higher coordination numbers, seven-coordinate species represent a commonly found, but poorly understood class. Theoretical studies imply that the three frequently found geometries[1,2]—D_{5h}, pentagonal bipyramid; C_{2v}, monocapped trigonal prism; C_{3v}, monocapped octahedron—are energetically close; facile interconversions are expected. Although dynamic NMR behavior has been observed in seven-coordination,[3] no definitive observation of the intimate mechanism for isomerization between idealized geometries has appeared. We report herein the preparation of $TaCl(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ (**1**) (dmpe = 1,2-(bisdimethylphosphino)ethane), its structure, and direct observation of the pentagonal bipyramid to monocapped trigonal prism interconversion.

Dropwise addition of 3.5 equiv of sodium naphthalene to a benzene solution of $(dmpe)_2TaCl_4$[4] which contained excess naphthalene gave a deep red solution. Removal of solvent and naphthalene in vacuo, chromatography (silica gel, THF eluent), and crystallization of the residue from toluene–hexane afforded **1** in poor yield. Treatment of a THF solution of **1** with an additional 2 equiv of sodium naphthalene and subsequent addition of HSO_3F or $MeOSO_2F$ gave $TaH(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ (**2**) and $TaMe(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ (**3**), respectively.[5]

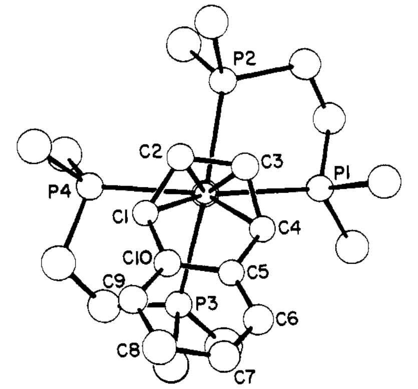

Figure 1. The molecular structure of $TaCl(\eta^4\text{-}C_{10}H_8)(dmpe)_2$ viewed along the Ta–Cl vector. Rotation of naphthalene by 45° about this vector yields the monocapped trigonal prismatic structure found for $TaCl(CO)_2(dmpe)_2$.[4] Ta–C distances (Å): Ta–C(1), 2.403 (9); Ta–C(2), 2.255 (9); Ta–C(3), 2.250 (9); Ta–C(4), 2.383 (9).

Crystals of $TaCl(\eta^4\text{-}C_{10}H_8)[(CH_3)_2PC_2H_4(CH_3)_2]_2$ are red monoclinic prisms: space group $P2_1/C$; $a = 10.343$ (3), $b = 10.281$ (3), $c = 24.642$ (7) Å; $\beta = 97.39$ (1)°; $Z = 4$. The 4019 independent reflections for which $I/\sigma(I) > 1.96$ were measured on a Syntex $P2_1$ diffractometer (crystal-monochromated Mo $K\alpha$ radiation). Full-matrix, least-squares refinement of positional and isotropic thermal parameters for all nonhydrogen atoms has converged to a conventional R factor[6] of 0.048.

The molecular structure of the complex (Figure 1) may be considered to be an approximate pentagonal bipyramid (cf. monocapped octahedral $TaH(CO)_2(dmpe)_2$[3h] and monocapped trigonal prismatic $TaCl(CO)_2(dmpe)_2$[4]) with the midpoints of the C(1)–C(2) and C(3)–C(4) bonds, Ta, P(1), P(4), and Cl forming the pentagonal plane (all with deviations < 0.24 Å), and P(2) and P(3) the apices of the bipyramid, the P(2)–Ta–P(3) angle being 154.0 (1)°. These distortions from the idealized pentagonal bipyramidal geometry are presumably a reflection of the bidentate nature of the ligands. In this complex, the diphosphine ligands are undisordered,[7] a probable consequence of steric interactions between the diphosphines and the naphthalene moiety. The angle between the η^4-diene residue of naphthalene (carbon atoms C(1) through C(4)) and the uncoordinated portion is 43.3°, which lies within the range reported (37.4–47.9°) for the few structurally characterized η^4-arene complexes.[8]

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **1** at −36 °C (Figure 2) is consistent with the ABCD pattern anticipated from the structural data. Coalescence to an A_4 system (55 °C) implies a process equilibrating P(1)–P(4). Similar behavior is observed for **2** and **3**.

At 70 °C the $^1H\text{-}\{^{31}P\}$ NMR spectrum shows an AA′BB′ pattern (δ 5.6, 4 H) assigned to H(6)–H(10) and a complex multiplet at δ 2.9 (H(2), H(3)),[9] consistent with the presence of an effective mirror plane in the naphthalene residue. The resonances attributable to H(1), H(4) are obscured by the dmpe methylene signals.[10] The observation of distinct resonances for bound and unbound naphthalene rings in the high-temperature limit rules out mechanisms involving transfer of the $TaClP_4$ group between ring systems. Further, at 70 °C the dmpe methyl groups occur as two distinct sets (δ 0.2, 12 H, and δ 0.5, 12 H): those directed toward Cl and those directed toward the diene fragment. This eliminates "arm-off, arm-on" processes and any mechanism involving migration of Cl or naphthalene about the P(1), P(2), P(3), P(4) plane.

On cooling to −50 °C the dmpe methyl and H(6)–H(9) resonances become more complex. The H(2), H(3) signal is