the same square patterns, so that the multiplet structure is preserved, but all peaks are positive. This multiplet is less prone to distortions and signal cancellation, and the comparison of in-phase and antiphase multiplets allows one to extract coupling constants with high accuracy.[16,17] Because the undesirable terms have vanished as if by a pixie's magic wand, we like to refer to this experiment as *p*ure *i*n-phase *c*orrelation *s*pectroscop*y* (PICSY).

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Dimerization of Aryl Radicals as a Termination Step in $S_{RN}1$ Aromatic Nucleophilic Substitution

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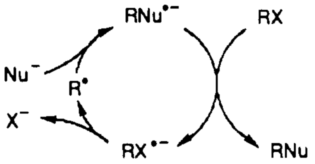
Aromatic nucleophilic substitution stimulated by light, electrodes, solvated electrons, and electrochemically generated electron donors is a well-documented reaction.[2] A large body of evidence exists to support that the reaction follows the $S_{RN}1$[3] reaction mechanism depicted by the following scheme:



in which the aryl radical, $R^\bullet$, derived from the cleavage of the anion radical of the substrate (RX) plays a central role in the formation of the substituted product (RNu). In this chain process, reduction of the aryl radical not only by the homogeneous or heterogeneous electron donors serving as initiators but also by the anion radicals included in the propagation loop ($RNu^{\bullet-}$ and to a lesser degree $RX^{\bullet-}$) has been recognized, on the basis of electrochemical evidence,[2b,d] as a major termination step. Another possible termination step is the coupling of two aryl radicals that would lead to the corresponding dimer:

$$2R^\bullet \rightarrow R{-}R$$

So far no such dimer has ever been found among the reaction products of $S_{RN}1$ substitution reactions. It is, however, interesting to note in this connection that a small amount of dimer has been detected in the addition of electrochemically generated cyanophenyl radicals on styrene,[4] a reaction that bears a close resemblance to the $S_{RN}1$ reaction. Although the absence of dimerization in $S_{RN}1$ reactions may be related to the likely smallness of the concentration of the $R^\bullet$ radical in the chain reaction, it remains surprising that it has never been detected under the largely varied experimental conditions employed heretofore.[5]

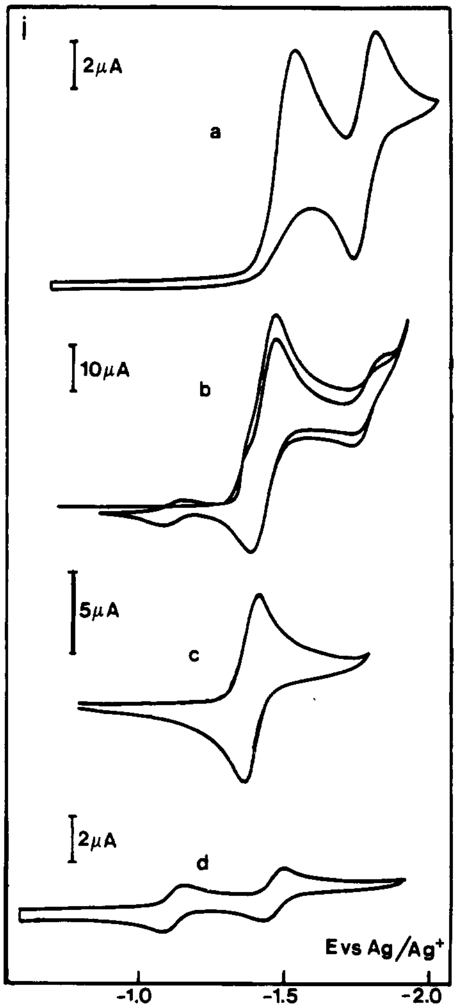


Figure 1. Cyclic voltammetry of 4-chlorobenzonitrile and reaction products in liquid NH_3 (+0.25 M KBr) at −38 °C at a 0.5 mm diameter gold disk electrode: (a) 4-chlorobenzonitrile alone in a 4.3 mM concentration; (b) 4-chlorobenzonitrile (35 mM) in the presence of 2-pyridinethiolate ions (47 mM); (c) 2-pyridyl 4-cyanophenyl sulfide (5.4 mM); (d) 4,4′-dicyanobiphenyl (0.5 mM). Scan rate: 0.2 V/s.

We have found that dimerization of aryl radicals may be, under appropriate experimental conditions, a quite efficient termination step yielding substantial quantities of the R–R dimer.

Figure 1 shows the cyclic voltammetry of 4-chlorobenzonitrile in liquid ammonia alone (a) and in the presence of 2-pyridinethiolate ions as the nucleophile (b). By comparison with the voltammogram of the substitution product (c), it appears that extensive substitution occurs in the diffusion layer. Some hydrogenolysis product (benzonitrile) also appears as demonstrated by the most negative wave in b. More important, a new reversible wave appears positive to the RX and RNu waves and located at the same potential as the first wave of 4,4′-dicyanobiphenyl (d). The second wave of the dimer is merged with the first wave of RNu. It should be noted that the concentration of RX that allows the formation of the dimer to be observed is high (35 mM), much higher than the concentrations used in past studies, and that the excess of nucleophile is small. The formation of the dimer was

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[1] (a) ESPCI. (b) Université de Paris.

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[5] (a) The absence of dimerization has even been taken recently as strong evidence against the reality of the $S_{RN}1$ mechanism which should, in the view of the authors, be replaced by an $S_{RN}2$ mechanism in which substitution would take place directly in the $RX^{\bullet-}$ anion radical with no intermediacy of the aryl radical. (d) Denney, D. B.; Denney, D. Z. *Tetrahedron* **1991**, *33*, 6577.

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checked by preparative-scale electrolysis. Constant current (60 mA) electrolysis at a stainless steel grid electrode (9 cm^2 geometric surface area, 324 mesh/cm^2) of a solution of 4-chlorobenzonitrile (0.06 M) and 2-pyridinethiolate ions (0.114 M) in liquid NH_3 (+ 0.25 M KBr) at −38 °C produced, after ca. 3 h, 39% of 4,4'-dicyanobiphenyl, 43% of 2-pyridyl 4-cyanophenyl sulfide, 8% of benzonitrile, and 3% of unreacted starting material. The dimer was identified after extraction from the electrolysis solution by comparison of its NMR spectrum with that of an authentic sample.

Formation of the dimer in comparable quantities was also found to occur in cyclic voltammetry with 4-iodo- and 4-bromobenzonitrile as well as with 4-chloropyridine using the same nucleophile. It was also observed with 4-iodobenzonitrile as the substrate and with thiophenoxide ions as the nucleophile.

As noted before, we have observed that large concentrations of the substrate and small excesses of the nucleophile are favorable factors for the formation of the dimer. The anion radicals of the substrates that have been selected for the present study all undergo rapid expulsion of the halide ion. It thus appears that rapid formation of $R^\bullet$ from $RX^{\bullet-}$ and rapid destruction of $RNu^{\bullet-}$ by large concentrations of RX in the propagation loop tend to decrease the reduction of $R^\bullet$ by $RNu^{\bullet-}$ and $RX^{\bullet-}$. $R^\bullet$ then mainly undergoes dimerization in competition with the attack of the nucleophile. The latter reaction should not, however, be too slow, otherwise the chain process would not be triggered in the solution and the reduction of $R^\bullet$ at the electrode surface would annihilate its chances to dimerize.

Work is now in progress to investigate in a more quantitative manner the exact effect of all the factors we have just evoked on the dimerization yield. For the moment we may conclude that it is possible to devise experimental conditions, making dimerization appear as an efficient termination step in aromatic nucleophilic substitutions. This observation provides further evidence of the intermediacy of the aryl radical in the reaction in full agreement with the $S_{RN}1$ mechanism.

Bis(triphenylphosphine)platinum Cycloheptadienynylium Fluoborate: The Tropylium Equivalent of Benzyne

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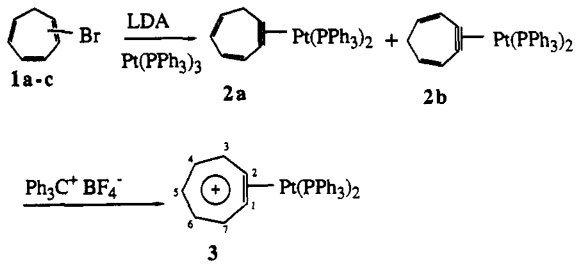
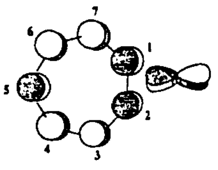
To our knowledge, there are no prior reports of the tropylium analogue of benzyne, either free[1,2] or complexed to a transition metal.[3] At this time we report the preparation and properties, including an X-ray diffraction crystal structure, of **3**, a Pt(0) complex of the cycloheptadienynylium ion, which we shall refer to as a complex of tropyne.

Preparation of the tropyne complex is outlined in Scheme I. Reaction of the mixture of 1-, 2-, and 3-bromocycloheptatriene (**1a–c**) with LDA led to, within the limits of detection by ^{31}P NMR, total regiochemical reversal from the reported reaction with *t*-BuOK; cycloheptadienyne complexes **2a** and **2b** were formed[4] (8:1) to the exclusion of the tetraene complex.[5] Hydride abstraction from the mixture of **2a** and **2b** with $Ph_3C^+BF_4^-$ gave the tropyne complex **3** as red, air-stable crystals.

The structure assigned to **3** is based on elemental analysis, ^1H, ^{13}C, ^{31}P, and ^{195}Pt NMR,[6] and an X-ray diffraction crystal structure. As expected, chemical shifts of both protons and carbons of the seven-membered ring are all shifted downfield relative to their dienyne counterparts **2a** and **2b**. However, the chemical shifts of the atoms that are not bonded directly to platinum are significantly upfield from those of the tropylium ion[7] (^1H, δ 9.55; ^{13}C, δ 160.6), indicating electron donation from platinum into the tropylium ring. This may be due to either or both a positive inductive effect and electron donation into the π-framework. Normally, symmetry limits back-bonding from a transition metal into the LUMO of the orthogonal π-bond of an alkyne to an ineffective δ-bond.[8] However, this is not the case for the tropyne complex because the tropylium ion has a vacant low-energy orbital[9] that can mix with a platinum "d" orbital as pictured in **4** (represented in resonance terms by **5**). This may be significant in the tropyne complex as evidenced by the ^{13}C resonance at C4/6 (lowest field resonance of remote carbons),[6] which correlates with the smallest LUMO coefficient and, hence, the lowest predicted electron density in **4** (0.12, HMO; 0.0, EHMO),[10] a Pt–C coupling constant (J_{Pt-C} = 458.5 Hz) that is larger than expected from strain[11] and is consistent with contribution from resonance forms such as **5**,[12,13] the ^{195}Pt chemical shift (−3788 ppm) which is further

Scheme I





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5a **5b**

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[6] Properties of **3**: ^1H NMR (300 MHz, CD_2Cl_2, δ) 7.2 (m, Ph), 7.4 (m, Ph), 7.66 (m, H3/7, $^3J_{Pt-H}$ = 51.9 Hz), 8.34 (m, H4/6), 8.64 (*t*, H5, $^3J_{H-H}$ = 10.0 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2, δ) 174.6 (dd, C1/2, $^1J_{Pt-C}$ = 458.5 Hz, $^2J_{P_{trans}-C}$ = 83.4 Hz, $^2J_{P_{cis}-C}$ = 5.0 Hz), 150.0 (d, C4/6, $^3J_{Pt-C}$ = 53.2 Hz, $^4J_{P_{trans}-C}$ = 10.5 Hz), 141.8 (s, C5), 135.6 (m, C3/7), 134.3, 133.1, 131.4 and 129.1 for Ph; ^{31}P NMR (121 MHz, CD_2Cl_2, δ, 85% H_3PO_4 as reference) 21.5 ($^1J_{Pt-P}$ = 3121.8 Hz); ^{195}Pt NMR (64 MHz, CD_2Cl_2, δ, Na_2PtCl_6 as reference) −3788. Anal. Calcd for $C_{43}H_{35}PtP_2BF_4 \cdot {}^1/_2CH_2Cl_2$: C, 55.68; H, 3.84. Found: C, 55.37; H, 3.80.

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[8] Cf. Coleman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 156.

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[11] For example, J_{Pt-C} = 318, 395, and 436 Hz for complexes of cycloheptyne, cyclohexyne, and cyclopentyne, respectively.[3]

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