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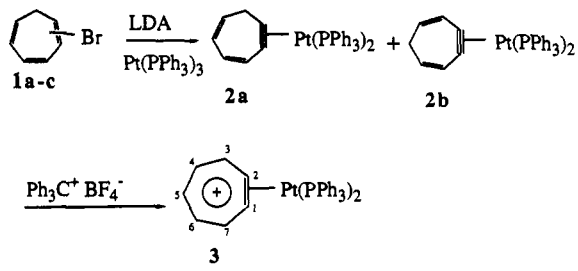
To our knowledge, there are no prior reports of the tropylium analogue of benzyne, either free[1,2] or complexed to a transition metal.[3] At this time we report the preparation and properties, including an X-ray diffraction crystal structure, of **3**, a Pt(0) complex of the cycloheptadienynylium ion,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

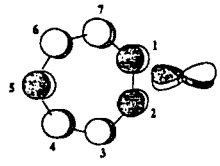
Preparation of the tropyne complex is outlined in Scheme I. Reaction of the mixture of 1-, 2-, and 3-bromocycloheptatriene (**1a–c**) with LDA led to, within the limits of detection by ^{31}P NMR, total regiochemical reversal from the reported reaction with *t*-BuOK; cycloheptadienyne complexes **2a** 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

Scheme I



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



4

5a **5b**

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

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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.

(7) (a) Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y. *J. Am. Chem. Soc.* **1972**, *94*, 3406. (b) Stewart, R. P., Jr.; Isbrandt, L. R.; Benedict, J. J.; Palmer, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 3215.

(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.

(9) Coulson, C. A.; Streitwieser, A., Jr. *Dictionary of π-Electron Calculations*; Pergamon Press Ltd: New York, 1965. EHMO shows nodes at C4 and C6.[13]

(10) W. R. Winchester, Trinity University, private communication.

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

(12) Chisholm, M. H.; Clark, H. C.; Ward, J. E. H.; Yasufuku, K. *Inorg. Chem.* **1975**, *14*, 893.

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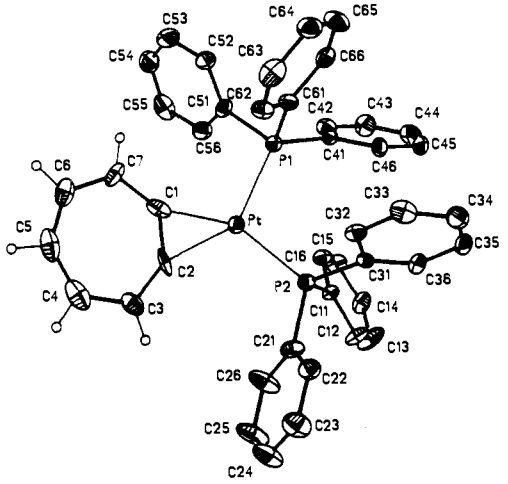


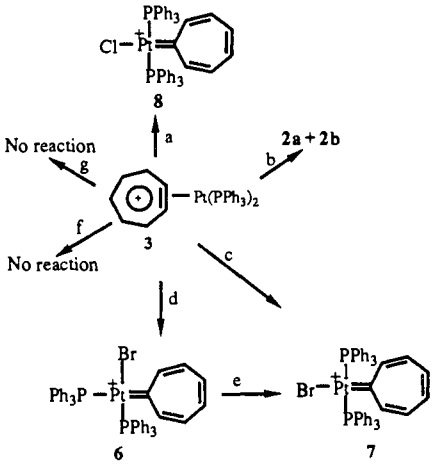
Figure 1. Thermal ellipsoid drawing of **3**, with 50% probability, showing the atom numbering scheme.

downfield than otherwise expected[14] [e.g., the Pt(II) complex **7** shows its Pt resonance at −4095 ppm],[13] and a reduction potential (−0.51 V vs Hg/HgCl) which is more negative than that of the tropylium ion (−0.29 V vs Hg/HgCl).[16]

Finally, the UV/vis spectrum of **3** shows a long wavelength absorption at 404 nm (log η = 3.44), 20 nm longer than the dienyne complex, suggesting communication between the platinum and the tropylium π-system. The crystal structure of **3** is shown in Figure 1. The seven-membered ring is planar [average atomic deviation from the least-squares plane is 0.02 (2) Å], and the platinum atom is at a distance of 0.274 (5) Å from this plane. It forms an angle of 7.8 (5)° with the plane containing Pt, C1, and C2. All C–C bonds in the seven-membered ring are equivalent within experimental error [bond average is 1.38 (2) Å]. This feature is also apparent in a Ni–benzyne complex[17] [bond averages: 1.367 (7) and 1.407 (7) Å] and a Zr–benzyne complex[18] [bond averages: 1.383 (9) Å]. However, it is in contrast to the short–long alternating C–C bonds observed in two Ta–benzyne complexes[19,20] and a Nb–benzyne complex.[20] The C–C triple bond [1.37 (2) Å] is longer than its counterparts in Pt–hexyne [1.297 (8) Å] and Pt–heptyne [1.283 (5) Å] complexes.[21] It is equivalent to the C–C triple bonds reported in the metal–benzyne complexes mentioned above. The Pt–C distances [2.00 (2) and 2.044 (13) Å] are similar to those in other metal–benzyne, metal–cyclohexyne, and metal–cycloheptyne complexes.[17-21]

The tropyne complex is relatively inert (Scheme II), showing no reaction with acetone or methanol at 70 °C for 12 h. It is also inert to acetonitrile at room temperature but, upon heating to 70 °C, is completely decomposed to a multitude of products in less than 2 h. It reacts cleanly and instantaneously with either HCl or HBr in THF to give Pt(II) complexes of cycloheptatrienylidene **7** and **8**;[13] in both cases only the trans isomer was detected. However, addition of HBr in CH_2Cl_2 gave first the cis-insertion product **6** (identified by ^1H and ^{31}P NMR), which slowly (ca. 4.8 h) isomerized to the trans isomer. The tropyne complex is also cleanly reduced to a mixture of **2a** and **2b**. Reductive coupling

Scheme II[a]



[a] (a) HCl in THF. (b) $KBEt_3H$ in THF. (c) HBr in THF. (d) HBr in CH_2Cl_2. (e) In CH_2Cl_2. (f) CH_3COCH_3, 70 °C, 12 h. (g) CH_3OH, 70 °C, 12 h.

reactions with alkenes and alkynes are under active investigation.

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Supplementary Material Available: Listings of details of the experimental procedures for the preparation of **2a**, **2b**, and **3**, ^1H, ^{13}C, 2D COSY, and C–H 2D NMR spectra of **3**, ^1H, 2D COSY, C–H 2D, and Pt–H 2D NMR spectra of **2a** and **2b**, and X-ray data for **3** (23 pages); table of observed and calculated structure factors for **3** (20 pages). Ordering information is given on any current masthead page.

(14) This conclusion is tenuous because ^{195}Pt NMR chemical shifts are not well understood.[15]

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EPR Evidence for Binuclear Mn(II) Centers in Rat Liver Arginase

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Arginase (L-arginine amidinohydrolase) catalyzes the hydrolysis of L-arginine to form L-ornithine and urea. A common feature of all arginases studied thus far is the requirement of divalent cations for activity. Mn^{2+} is the physiological cofactor, although activation of the enzyme by Co^{2+}, Ni^{2+}, Fe^{2+}, VO^{2+}, and Cd^{2+} has been reported.[1] The arginases from the *Agrobacterium* TiC58 plasmid,[2] *Neurospora crassa*,[3] and *Rhodobacter capsulatus* E1F1 cells[4] are specifically activated by Mn^{2+}, while the enzyme isolated from the thermophilic *Bacillus caldovelox* contains ≥1 Mn/subunit.[5] The function of the metal ion in the catalytic mechanism and/or structure of the protein is unknown, although recent work

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