atm/85 °C) for 6 h, compound 1 was reformed quantitatively.

The facile carbon–sulfur bond formation that occurred in the formations of 1 and 2 suggests that similar processes could be important on sulfur-contaminated metal surfaces and that the interactions of sulfur with the key hydrocarbyl intermediate formed in Fischer–Tropsch and related catalytic processes may play a role in the inhibition of these reactions by sulfur.

Supplementary Material Available: Tables of crystal data, positional and thermal parameters, and selected interatomic distances and angles (11 pages); tables of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

Alkyne Reactions with Cyclopalladated Complexes

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Summary: A general scheme is proposed for reactions of cyclopalladated complexes with alkynes. Successive insertions of alkyne units form a series of complexes which in turn may reductively eliminate palladium or rearrange. Four types of products are known, additional examples of one type and two new types are reported in our study of reactions of ionic cyclopalladated complexes. These last reactions are useful for preparing 2-substituted cinnolinium salts and isoquinolinium salts. A double alkyne insertion occurs with some complexes to form naphthalene derivatives, and a cyclopentadiene ring is formed from a triple alkyne insertion in another example.

The literature reports several reactions of alkynes with cyclopalladated complexes. Cyclopalladated complexes of N,N-dimethylbenzylamine,[1] 8-methylquinoline,[1] benzo-[h]quinoline,[1] and 2-benzylpyridine[2] for example, generally have given various organopalladium compounds as products with alkynes. The reported reactions were all carried out with the covalent cyclopalladated chloride dimers, acetate dimers, or palladium complexes having two chelating organic ligands.[3] We have now found that converting the cyclopalladated complexes to the presumed

ionic tetrafluoroborates significantly activates the complexes and reactions with alkynes occur even at room temperature. Different types of products than previously reported are obtained in some of these reactions.

Our initial results combined with the literature reports strongly suggest a general reaction scheme that indicates the relationships between all of the various products so far obtained from the reactions. Scheme I below shows the proposed reactions illustrated with the N,N-dimethylbenzylamine complex. A series of single alkyne insertions is proposed which yield palladium complexes at each step. These complexes either may insert another alkyne unit or may undergo palladium(0) elimination or rearrangements to other products. Substantial evidence now exists to support the proposed steps although not all with the same cyclopalladated complex. Which of the possible paths a given complex will take in reacting with an alkyne will depend upon steric and electronic factors in both the complex and alkyne and upon the concentration of the reacting alkyne as well as upon the reaction temperature if the activation energies of the various possible reactions are significantly different.

Complexes of the type II,[1,3] IV,[1] and V[2] have been reported to be formed in alkyne reactions. One product of type III has been reported employing hexafluorobutyne as the reactant[1] (demethylation also occurred in the example), and we now report several more examples of this reaction. We have also found examples of the formation of product VII and complex IX.

Treatment of the cyclopalladated chloro dimer from azobenzene[5] with silver tetrafluoroborate in nitromethane solution rapidly causes silver chloride to precipitate and a bright red solution is formed. Filtration and evaporation of the solvent leaves a viscous red oil which, so far, has resisted attempts at crystallization. The less reactive bis(acetonitrile) complex, however, is easily obtained as stable yellow crystals from acetonitrile solution. The reaction of the "(azobenzene)palladium tetrafluoroborate" in nitromethane with excess diphenylacetylene at room temperature led to the formation of 35% of 2,3,4-triphenylcinnolinium tetrafluoroborate and, presumably, polyinsertion products as viscous, nonseparable oils. The yield of the cinnolinium salt is 87% if the diphenylacetylene (0.8 M in nitromethane) is added slowly to the stirred palladium salt in nitromethane solution ($\sim$0.13 M) at 100 °C (over a period of 3.5 h; eq 1). (This procedure
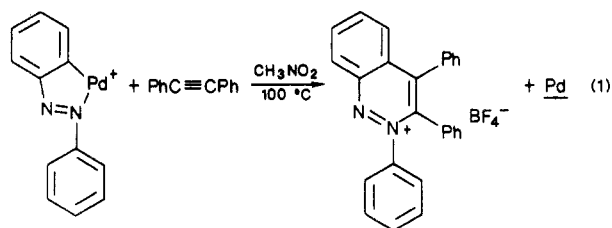
eliminates the competition of $k_2[\text{PhC}{\equiv}\text{CPh}]$ with k_1 in Scheme I.) The structure of the product was determined by X-ray crystallography. Similar yields of the expected cinnolinium salts were obtained from 3-hexyne (83%) and from dimethyl acetylenedicarboxylate (80%). This reaction is a useful, new method for preparing some of the very rare, 2-substituted cinnolinium salts.

The same type of reaction occurs between 3-hexyne and cyclopalladated N-benzylidene-o-toluidine[6] and N-

(1) Bahsoun, A.; Dehand, J.; Pfeffer, M.; Zinsius, M. *J. Chem. Soc., Dalton Trans.* **1979**, 547.

(2) Maassarani, F.; Pfeffer, M.; LeBorgne, G. *J. Chem. Soc., Chem. Commun.* **1986**, 489.
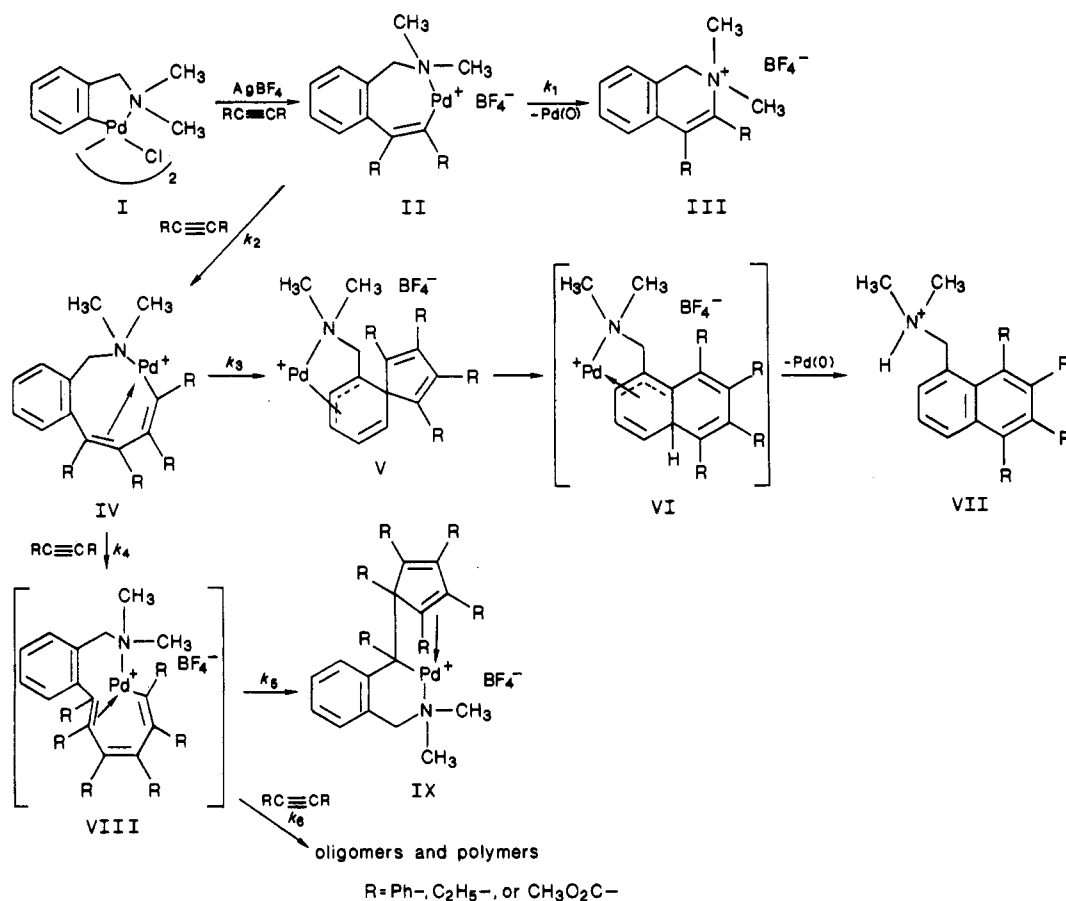
(3) Arlen, C.; Pfeffer, M., Bars, O.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1535.

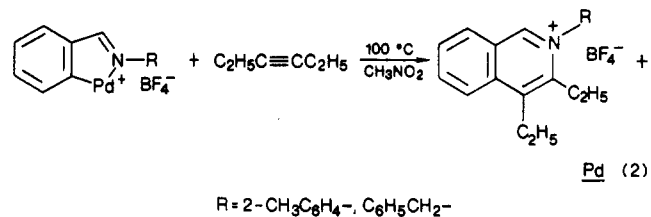(4) Hart, D. W.; Bau, R.; Chao, C. H.; Heck, R. F. *J. Organomet. Chem.*, **1979**, *179*, 301.

(5) Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272.

(6) Onone, H.; Moritani, I *J. Organomet. Chem.* **1972**, *43*, 431.

Scheme I

R = Ph-, C₂H₅-, or CH₃O₂C-

benzylidenebenzylamine[7] tetrafluoroborate salts to form isoquinolinium salts as products (eq 2) in fair yields (~50%). This procedure provides a new route to iso-


Pd (2)

R = 2-CH₃C₆H₄-, C₆H₅CH₂-

quinolinium salts which may prove to be valuable also because of the ease of formation of functionalized palladium complexes and, presumably, subsequently the substituted isoquinolinium salts.

Reaction of 3-hexyne with the tetrafluoroborate of cyclopalladated *N,N*-dimethylbenzylamine,[8] on the other hand, at room temperature gives 55% of a tetraethylnaphthalene derivative presumably via path k_3 of Scheme I (eq 3). Path k_1 may be unfavorable in this instance for steric reasons. The naphthalene structure also was established by X-ray crystallography.

+ Pd (3)
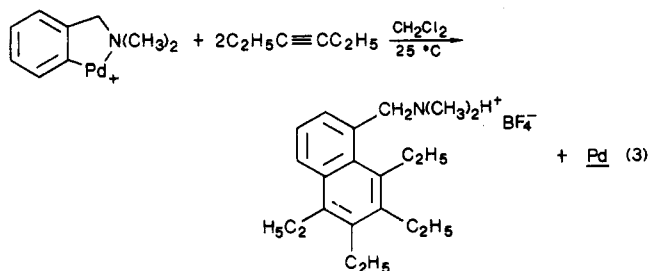
Finally, the tetrafluoroborate of cyclopalladated 8-methylquinoline[9] and 3-hexyne at room temperature yield a complex of type IX (20%). A crystal structure of this product proved it to have the structure shown in eq 4. This reaction is remeniscent of the 2-butyne trimerization with palladium chloride reported many years ago by Maitlis.[10]

+ 3C₂H₅C≡CC₂H₅ →   (4)
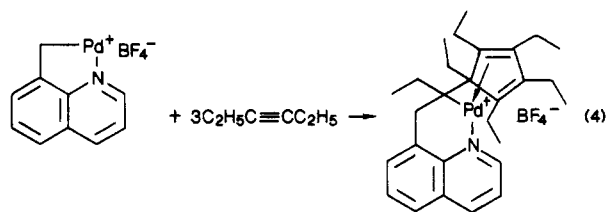
We have looked briefly at the reactions of the cyclopalladated azobenzene tetrafluoroborate complex with alkenes. While the cyclopalladated chloro dimer is very unreactive,[4] the tetrafluoroborate reacts at room temperature with styrene to form a 90% yield of a new dimer, 2,3-diphenyl-1-butene, with 1-pentene to form 2-pentene and with methyl acrylate at 50 °C to form polymer (eq 5). An (azobenzene)palladium hydride catalyst seems to best explain the results, but the mechanism of formation of the presumed hydride is not clear. In the styrene reaction, the sterically large azobenzene group must cause the insertion of the second styrene to go opposite from the usual direction. Both tetrakis(acetonitrile)palladium(II) tetrafluoroborate[11] and a fluoroborate from tri-*n*-butyl-
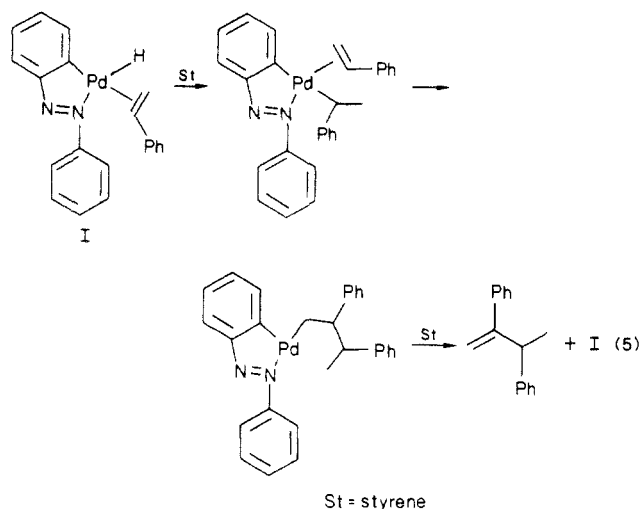
(7) Albert, J.; Granell, J.; Sales, J. *J. Organomet. Chem.* **1984**, *273*, 393.
(8) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.

(9) Hartwell, G. E.; Lawrence, R. V.; Smas, M. J. *J. Chem. Soc. Chem. Commun.* **1970**, 912.
(10) Reinheimer, H.; Moffat, J.; Maitlis, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2285.
(11) Sen, A.; Lai, T.-W. *Organometallics* **1983**, *2*, 1059.

phosphine π-allylic palladium(II) chloride[12] dimerize styrene to 1,3-diphenyl-1-butene.

We are currently studying the scope of the alkyne and alkene reactions with various cyclopalladated complexes.

(12) Grenouillet, P.; Neibecker, D.; Tkatchenko, I. *Organometallics* 1984, *3*, 1130.

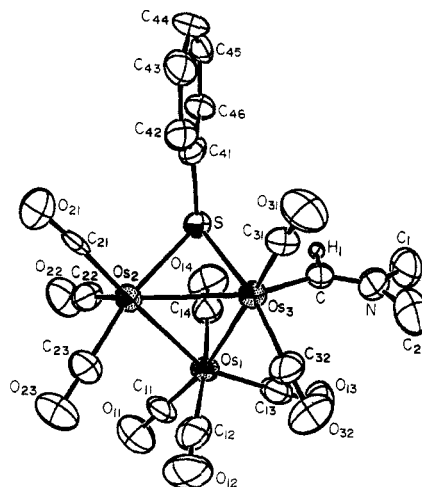# Novel Ligand Transformations in Cluster Complexes. α-CH Bond Activation in a Secondary Carbene Ligand in a Triosmium Cluster

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Summary: The carbene cluster complex $Os_3(CO)_9[C(H)NMe_2](\mu\text{-SPh})(\mu\text{-H})$ (2) has been synthesized in 66% yield by the reaction of $Os_3(CO)_{10}(\mu\text{-SPh})(\mu\text{-H})$ with $CH_2(NMe_2)_2$. Photodecarbonylation of 2 leads to formation of the compound $Os_3(CO)_8(\mu\text{-C}=NMe_2)(\mu\text{-SPh})(\mu\text{-H})$ (3) in 37% yield by an α-CH bond activation in the carbene ligand.

The ability of transition-metal cluster compounds to produce transformations in small molecules by interactions at two or more metal sites has been one of the most exciting and important aspects of the chemistry of these compounds.[1] The intramolecular activation of C–H bonds by clusters is a topic that has received considerable attention.[2] An understanding of these transformations in clusters could play an important role in developing a unified understanding of Fischer–Tropsch and related catalytic processes.[3] We have recently reported that the cluster $Os_3(CO)_9(\mu_3\text{-CO})(\mu_3\text{-S})$ reacts with trimethylamine

(1) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985**, *33*, 127.

(2) (a) Cree-Uchiyama, M.; Shapley, J. R.; St. George, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 1316. (b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726. (c) Green, M.; Hankey, D. R.; Murray, M.; Orpen, A. G.; Stone, *J. Chem. Soc., Chem. Commun.* **1981**, 689. (d) Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4542.

Figure 1. An ORTEP diagram of $Os_3(CO)_9[C(H)NMe_2](\mu\text{-SPh})(\mu\text{-H})$ (2) showing 50% probability thermal ellipsoids. The hydrogen atom H(1) is shown with an arbitrarily assigned temperature factor of $B = 1.0$ Å².

at 125 °C to activate two C–H bonds on one of the methyl groups to form the new cluster $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-S})(\mu\text{-H})_2$ (1) which contains a secondary (dimethylamino)carbene ligand.[4] We have now found that $Os_3(CO)_{10}(\mu\text{-SPh})(\mu\text{-H})$ reacts with bis(dimethylamino)methane to yield the new carbene cluster complex $Os_3(CO)_9[C(H)NMe_2](\mu\text{-SPh})(\mu\text{-H})$ (2) which upon photoinduced decarbonylation undergoes an intramolecular α-CH bond activation that transforms the terminally coordinated carbene ligand into a bridging (dimethylamino)carbyne ligand.

The reaction of 100 mg of $Os_3(CO)_{10}(\mu\text{-SPh})(\mu\text{-H})$ with 3.5 mL of $CH_2(NMe_2)_2$ in 100 mL of heptane solvent for 11 h at reflux yields 39 mg (66% based on the amount of $Os_3(CO)_{10}(\mu\text{-SPh})(\mu_3\text{-H})$ consumed) of compound 2. Compound 2 was characterized by IR and ¹H NMR spectroscopies and elemental and single-crystal X-ray diffraction analyses.[5–7] An ORTEP diagram of the molecular structure of 2 is shown in Figure 1.[8] The molecule consists of a triangular cluster of three osmium atoms that has one edge bridged by a phenylthio ligand. A hydride ligand (not observed crystallographically) is believed to bridge the Os(2)–Os(3) bond on the side of the cluster opposite

(3) (a) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (b) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1981**, *103*, 1297; **1980**, *102*, 6181. (c) Biloen, P; Helle, H. N.; Sachtler, W. M. H. *J. Catal.* **1979**, *58*, 95.

(4) Adams, R. D.; Kim, H. S.; Wang, S. *J. Am. Chem. Soc.* **1985**, *107*, 6107.

(5) Compound 2 is air-stable and was isolated by TLC on silica gel using a 10:90 CH_2Cl_2/hexane solvent mixture. IR in hexane solvent ($\nu(CO)$, cm⁻¹): 2092 (m), 2052 (m), 2013 (vs), 2002 (w), 1996 (m), 1966 (w), 1940 (w). ¹H NMR (CD_2Cl_2, δ): 11.71 (s, 1 H), 7.22 (m, 5 H), 3.61 (s, 3 H), 3.56 (s, 3 H), –17.24 (s, 1 H). Elemental Anal. Calcd (Found): C, 21.80 (21.91); H, 1.32 (1.31); N, 1.41 (1.42).

(6) Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer by using Mo Kᾱ radiation. Structure solutions and refinements were performed on a Digital Equipment Corp. MICROVAX I computer by using the Molecular Structure Corp. TEXSAN program library. The data were corrected for absorption.

(7) Crystals of 2 were grown by slow evaporation of solvent from CH_2Cl_2/hexane solutions at –20 °C. Compound 2 crystallizes in the monoclinic crystal system: space group $P2_1/n$, $a = 15.841$ (3) Å, $b = 10.246$ (2) Å, $c = 15.594$ (3) Å, $\beta = 111.23$ (1)°, $Z = 4$, $\rho_{calcd} = 2.58$ g/cm³. The structure was solved by direct methods (MULTAN) and was refined (2800 reflections) to the final values of the residuals $R = 0.0357$ and $R_w = 0.0435$.

(8) Selected interatomic distances (Å) and angles (deg) for 2 are as follows: Os(1)–Os(2) = 2.8711 (9), Os(1)–Os(3) = 2.877 (1), Os(2)–Os(3) = 2.8640 (9), Os(3)–C = 2.02 (2), C–N = 1.28 (2), C–H(1) = 1.06; Os(1)–Os(3)–C = 93.6 (4), Os(2)–Os(3)–C = 135.1 (4), Os(3)–C–N = 137 (1).