in ethanol effects complete conversion in 30 min, acid alumina causes rapid isomerization, etc. Both analyses and spectra confirm the assigned structure. This reaction finds analogy in the highly facile acid-induced ring opening of the spiropentene **2** to the triafulvene **9**.[6]

The nature of the intermediate(s) that leads to heptafulvalene and spirononatriene is, of course, questionable.[11] However, whatever its structure, the products that it gives rise to are those anticipated for a carbene (dimer formation) of low electrophilicity (no reaction with alkenes) and relatively high nucleophilicity (reaction with electrophilic double bonds).

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(11) Reaction of heptafulvalene with dimethyl fumarate in a reaction analogous to that proposed by Lemal[3] to explain the products of reaction of electrophiles with tetraaminoethylenes was independently excluded as the source of the spirononatriene.

(12) (a) Alfred P. Sloan Fellow, 1963–1967. (b) Gulf Oil Fellow, 1966–1967.

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Reversible Combination of Molecular Nitrogen with a Cobalt Complex. Exchange Reactions of Nitrogen–Tris(triphenylphosphine)cobalt with Hydrogen, Ethylene, and Ammonia

Sir:

Previously we reported that molecular nitrogen combines with a cobalt complex in the reaction of cobalt acetylacetonate, diethylaluminum monoethoxide, and triphenylphosphine carried out in an atmosphere of nitrogen.[1] We wish to report now on some exchange reactions of the isolated complex, nitrogen–tris(triphenylphosphine)cobalt (I), with molecular hydrogen, ethylene, and ammonia. Recently, ruthenium[2,3] and iridium[4] complexes, which are combined with molecular nitrogen, have been reported, but no report has been made, as far as we know, on the reaction of a nitrogen-coordinated complex with these gases.

When a benzene solution of nitrogen–tris(triphenylphosphine)cobalt (I) is swept or shaken with purified hydrogen gas, the original red color changes to yellow with a loss of molecular nitrogen from the complex, as proved by infrared and mass spectrometry. The sharp strong band at 2088 cm^{-1} assigned to the stretching vibration of the coordinated nitrogen molecule disappears rapidly with the appearance of new bands at about 1940 and 1760 cm^{-1}. Sweeping the benzene solution of I with argon gas does not affect the original spectrum at all. On concentrating the yellow benzene solution, light yellow crystals are isolated which can be recrystallized from toluene. *Anal.* Calcd for $C_{54}H_{47}P_3Co$ (II): C, 76.50; H, 5.59. Found: C, 76.72; H, 6.00; N, 0. Thermal decomposition of the yellow complex II releases hydrogen and benzene. On sweeping the yellow solution of II with nitrogen, the ν_{N_2} band at 2088 cm^{-1} resumes the original intensity and the solution regains its initial red color. The cycle can be repeated many times, showing a reversible equilibrium.

$$\underset{\text{I}}{[(C_6H_5)_3P]_3Co \cdot N_2} + H_2 \rightleftharpoons \underset{\text{II}}{[(C_6H_5)_3P]_3CoH_2} + N_2 \qquad (1)$$

On sweeping the benzene solution of I with deuterium, a band is observed at 1260 cm^{-1} which may be assigned to a Co–D stretching vibration which is shifted from the band of Co–H stretching vibration at 1760 cm^{-1} by a factor of 1.4. The band at 1940 cm^{-1} was not observed in the spectrum of the benzene solution swept with deuterium, but no corresponding new band due to deuterium substitution appeared. The origin of the band at 1940 cm^{-1} is not clear at the moment.

When a benzene solution of I is swept with purified ethylene, the original red color darkens with the loss of the coordinated nitrogen molecule. The ν_{N_2} band at 2088 cm^{-1} disappears and new bands, which may be assigned to the C–H stretching vibration of the coordinated ethylene molecule, appear at about 2950 and 2850 cm^{-1}. Similar bands are observed in the spectrum of $[(C_6H_5)_3P]_2Ni \cdot C_2H_4$ prepared according to Wilke and Hermann.[5] On passing nitrogen through the solution, these bands disappear and the ν_{N_2} band resumes the original intensity, suggesting a reversible exchange reaction of the type

$$\underset{\text{I}}{[(C_6H_5)_3P]_3Co \cdot N_2} + C_2H_4 \leftrightarrows \underset{\text{III}}{[(C_6H_5)_3P]Co \cdot C_2H_4} + N_2 \qquad (2)$$

Tris(triphenylphosphine)cobalt coordinated with ethylene (III) can be isolated by the reaction of cobalt acetylacetonate, triphenylphosphine, and diethylaluminum monoethoxide in an argon atmosphere.[6] Combination of nitrogen with cobalt also takes place in the reaction of tris(triphenylphosphine)methylcobalt[1] with nitrogen gas.

Analogous reversible reaction of the nitrogen–cobalt complex is observed with ammonia as indicated by the reversible change of the ν_{N_2} band. The complex reacts irreversibly, however, with carbon monoxide and carbon dioxide. The details will be reported later.

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(1) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967).

(2) A. D. Allen and C. V. Senoff, *ibid.*, 621 (1965).

(3) A. E. Shilov, A. K. Shilova, and Yu. G. Borodko, *Kinetika i Kataliz*, 7, 768 (1966).

(4) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **88**, 3459 (1966); **89**, 169 (1967); **89**, 844 (1967).

(5) G. Wilke and G. Hermann, *Angew. Chem.*, 74, 693 (1962).

(6) Unpublished results.

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Reaction of Benzyne with Benzene. Effect of Silver Ion

Sir:

The decomposition of suspensions of benzenediazonium-2-carboxylate (**1**) in excess benzene at 45° is reported[1] to yield benzobarrelene (**2**), benzocyclooctatetraene (**3**), and biphenyl (**4**) (*cf.* run 8, Table I). The products were postulated to occur by 1,4 addition,[1] 1,2 addition (followed by valence bond isomerism),[1] and insertion[2a] reactions of benzyne (from **1**) on benzene, respectively. These are the "accepted" prod-

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(1) R. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, **85**, 1798 (1963).