The Preparation of Palladium–Olefin Complexes from Palladium Vapour

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Summary The reactions of palladium atoms with olefins have been studied by low-temperature i.r. spectroscopy and the most stable compounds observed, bis(cyclo-octa-1,5-diene)palladium and tris(bicyclo[2.2.1]heptene)-palladium have been prepared from palladium atoms on a gram scale.

Following the preparation of bis(cyclo-octa-1,5-diene)-iron(0)[1] we have attempted the synthesis of other unstable olefin–metal complexes from reactions of metal atoms. Low temperature i.r. spectroscopy has been used for detecting the complexes on a micro-scale and for estimating their thermal stability. Compounds of sufficient thermal stability have then been made on a gram scale. We now report reactions with palladium atoms which have led to the first syntheses of bis(cyclo-octa-1,5-diene)palladium and tris(bicyclo[2.2.1]heptene)palladium, compounds now obtainable by conventional reductive methods.[2]

For the i.r. studies, thin films of the known nickel complexes, bis(cyclo-octa-1,5-diene)nickel,[3] tris(bicyclo[2.2.1]-heptene)nickel,[4] and tris(ethylene)nickel,[4] were prepared by condensing a few milligrams of nickel vapour with a 30-fold mole excess of the ligand vapour on a caesium iodide window kept just cold enough to act as an efficient cryo-pump for the ligand vapour. The window was then warmed to a temperature at which excess ligand could be pumped away at 10^{-4} Torr leaving a transparent film of the nickel complex. The i.r. spectra of the films over the range 400—3500 cm^{-1} showed sharp, well-resolved bands. The experiments were repeated using palladium vapour in place of nickel with each of the ligands. The spectra obtained were virtually identical to those with nickel in the number and intensity of the bands; shifts of 0—10 cm^{-1} were observed between comparable bands in the complexes from the two metals. In the complexes with ethylene, two bands at 1513 cm^{-1} and 1522 cm^{-1} were observed for palladium in place of one band at 1510 cm^{-1} for nickel. The results strongly suggested that the palladium complexes were isostructural with the nickel complexes, *i.e.* that the compounds are bis(cyclo-octa-1,5-diene)palladium, tris-(bicyclo[2.2.1]heptene)palladium, and tris-(ethylene)palladium. In a thin film under vacuum the compounds were observed to decompose to palladium metal at −20 °C, 0 °C and −70 °C respectively. Nickel atoms and palladium atoms were also each condensed with propene. The i.r. spectra of the condensates warmed to −100 °C were very similar, although the results do not permit an assignment of the stoicheiometry of those metal–propene complexes which decomposed above −80 °C.

Palladium atoms react almost quantitatively with cyclo-octa-1,5-diene in methylcyclohexane solution at −120°. Addition of trimethylphosphite to the cold solution gives an 80% yield of $\text{Pd}[\text{P(OMe)}_3]_4$ based on the palladium vapour condensed. However, bis(cyclo-octa-1,5-diene)palladium is so labile that it has been isolated only in about 20% yield from the above solution as colourless crystals [thermal decomposition to palladium and cyclo-octa-1,5-diene gave $\text{Pd(C}_8\text{H}_{12})_{1\cdot 90}$, CH determinations gave $[\text{Pd(C}_8\text{H}_{12})_{1\cdot 93}]$.

Colourless crystals of tris(bicyclo[2.2.1]heptene)Pd were obtained in about 40% yield after condensing palladium vapour on a gram scale with excess bicyclo[2.2.1]heptene at −196°. The ^{1}H n.m.r. spectrum ([^{2}H$_8$]-toluene, −30°) showed resonances at δ 3·99 (C*H*=C*H*), 2·99 (C*H*), 1·60 (C*H*$_2$-C*H*$_2$) and 0·44 (bridging C*H*$_2$); the ^{13}C n.m.r. spectrum showed resonances at 27·3 (*C*H), 41·4 (bridging *C*H$_2$), 42·8 (*C*H$_2$-*C*H$_2$), and 82·5 p.p.m. (*C*H=*C*H).

Both bis(cyclo-octa-1,5-diene) palladium and tris-(bicyclo[2.2.1]heptene)palladium react with dibenzylidene acetone to give the known $\text{Pd}_2\text{(DBA)}_3$ (isolated as the chloroform adduct[5]); direct reaction of palladium atoms with dibenzylidene acetone in solution also yields $\text{Pd}_2\text{(DBA)}_3$ in moderate yield.

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