Simple Allene Complexes of Transition Metals

By JOHN A. OSBORN

(*Department of Chemistry, Harvard University, Cambridge, Massachusetts* 02138)

INTEREST has recently been shown in the interaction of allenes with transition-metal complexes.[1,2] However, although postulated as intermediates in certain reactions (*e.g.* insertion of allene into a Pd–Cl bond to form a chloro-allyl complex), no simple allene complexes have been isolated.* We have studied the interaction of allene with some low-valent platinum metal complexes, and have isolated some simple allene complexes.

When a degassed benzene solution of $Pt(PPh_3)_4$ is treated with allene, the yellow solution immediately loses colour, and, on standing, or on addition of ethanol, white crystals of the complex, $Pt(PPh_3)_2(CH_2{=}C{=}CH_2)$, are deposited in high yield.† The complex is stable in air and does not dissociate in the crystalline state, but allene can be displaced from a solution at room temperature by treatment with excess of PPh_3. The following equilibrium is set up, and can be observed by alternatively flushing the benzene solution with allene and argon:

$$Pt(PPh_3)_4 + CH_2{=}C{=}CH_2 \rightleftharpoons Pt(PPh_3)_2(CH_2{=}C{=}CH_2) + 2PPh_3$$

The mull spectrum shows a band at 1680 cm.$^{-1}$ attributable to a $\nu(C{=}C)$, which is shifted < 250 cm.$^{-1}$ downfield from the "double bond" in free allene. The n.m.r. spectrum in $CDCl_3$, although incompletely resolved owing to the low solubility of

---

* The substituted allene complex, tetracarbonyl tetramethylalleneiron has been recently isolated and shows valence tautomerism in solution (see ref. 2.)

† Satisfactory elemental analyses have been obtained for all stable compounds. Molecular weight measurements were made cryoscopically in benzene.

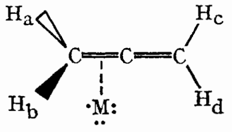
the complex, shows three bands (apart from the PPh_3 resonances) at τ 8·00, 5·57, and 5·33, relative intensities 2 : 1 : 1 due to the bonded allene.

Similar treatment of the analogous palladium complex with allene gave crystals of $[Pd(PPh_3)_2]_n$; co-ordinated allene was indicated by neither the i.r. nor the n.m.r. spectrum. This complex was previously isolated from the interaction of $Pd(PPh_3)_4$ with vinyl chloride,[3] and in this case its formation may well have occurred *via* a labile allene complex.

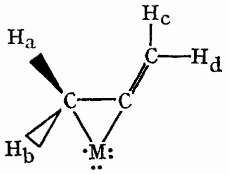
When allene is bubbled through a dichloromethane solution of $Rh(PPh_3)_3Cl$, yellow crystals of the complex, $Rh(PPh_3)_2Cl(CH_2{=}C{=}CH_2),\frac{1}{2}CH_2Cl_2$ are deposited. Solutions of this complex are stable in air for several hours, but the allene can be slowly displaced by PPh_3 at room temperature, and readily yields *trans*-$Rh(PPh_3)_2COCl$ with carbon monoxide. No reaction occurs on treatment of a benzene solution of the complex with molecular hydrogen, indicating, as previously suggested,[4] that the catalytic hydrogenation process does not go *via* hydrogenation of the olefin complex. The i.r. spectrum shows a band at 1730 cm.$^{-1}$ attributable to $\nu(C{=}C)$. The n.m.r. spectrum in $CDCl_3$ shows (apart from triphenylphosphine and dichloromethane resonances) unresolved multiplets due to the allene at τ 9·47, 5·92, and 5·65, relative intensities 2 : 1 : 1.

The d^8 Ir^I complex, *trans*-$Ir(PPh_3)_2COCl$, does not yield a stable allene complex although there is spectroscopic evidence that a weak complex is present in an excess of allene. However, orange solutions of the more nucleophilic species, $Ir(diphos)_2^+$ cation, change immediately to pale yellow in presence of allene and white crystals of the complex, $Ir(diphos)(CH_2{=}C{=}CH_2)^+Cl^-$ can be isolated. This reaction, however, is readily reversible in solution, and allene is lost on pumping in the crystalline state. The complex is unstable in air, being rapidly attacked by oxygen to yield the known species $Ir(diphos)_2O_2^+$ cation.[5] The mull i.r. spectrum of a partially decomposed sample, shows, apart from a band due to free allene, a band at 1640 cm.$^{-1}$, attributable to the complexed species.

These complexes are of some structural interest. In most cases where simple allene complexes have been postulated as reaction intermediates, the bonding of the allene to the metal has been shown as π-bonding as in (A):



(A)



(B)

However, allene is isoelectronic with carbon disulphide, and a bonding form as in (B), analogous to that found for $Pt(PPh_3)_2CS_2$[6] is also possible or could contribute to the overall bonding. The i.r. data do not readily distinguish between these two formal structural geometries. It would be expected that the band at *ca.* 1940 cm.$^{-1}$ in free allene would be appreciably shifted to lower frequencies on co-ordination as in (A), although the magnitude of the shift is somewhat larger than would be expected for simple π-bonding. Also the "free" double bond in (B) would be expected to occur at *ca.* 1700 cm.$^{-1}$ (*e.g.* as in methylenecyclopropane[7]), it being directly attached to the three-membered ring system. The n.m.r. data, however, point to (B) as a major contributor to the bonding. It is found in both the platinum and the rhodium complexes, $H_a \equiv H_b$, showing that a mirror plane bisects the allene in these complexes. More significant is that these protons are shifted appreciably to high field, the rhodium complex particularly showing a resonance well in the aliphatic region. This indicates that these complexes are best regarded as derivatives of Pt^{II} and Rh^{III}, the allene bonding *via* two σ bonds, as found in certain complexes of C_2F_4, O_2, and $(CN)_2C_2(CN)_2$. There is no evidence for any degenerate valence-tautomerism in these complexes as found in tetramethylalleneiron tetracarbonyl.[2] It is possible that with a first-row transition metal and with electron-releasing groups on the allene, the main bonding contributor is (A). This π-bonding molecule would be more likely to facilitate intramolecular rearrangements, which would not be possible in a σ-bonded structure as in (B).

This work has been supported by the William F. Milton Fund.

(*Received, July 23rd,* 1968; *Com.* 996.)

---

[1] R. Ben-Shoshan and R. Petit, *Chem. Comm.*, 1968, 247; A. Nakamura, *Bull. Chem. Soc. Japan*, 1966, **39**, 543; R. G. Schultz, *Tetrahedron*, 1964, **20**, 2809; M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1687.

[2] R. Ben-Shoshan and R. Petit, *J. Amer. Chem. Soc.*, 1967, **89**, 2231.

[3] P. Fitton and J. E. McKeon, *Chem. Comm.*, 1968, 4.

[4] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

[5] L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, 1966, **88**, 5324.

[6] M. Baird, G. Hartwell, jun., R. Mason, A. I. M. Rae, and G. Wilkinson, *Chem. Comm.*, 1967, 92.

[7] J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, 1953, **75**, 3344.