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Acetylenic complexes of palladium*

Complexes of transition metals in which an acetylene monomer is coordinated to the metal have been reported for vanadium[1], chromium[2], molybdenum[3,4,6], tungsten[5,6], manganese[7,8], rhenium[9], iron[10,11], cobalt[12,13], rhodium[14], iridium[15], nickel[11,13,16,17], platinum[8,18,19] as well as copper[20] and silver[20]. We now report the synthesis of some palladium–acetylene complexes.

Platinum forms two types of complexes with acetylenes, one of the type $RC_2R'Pt^{II}Cl_2X$ (I, $X = Cl^-$, amine, etc.) where R and R′ are bulky groups such as tert-butyl[18]. In addition, complexes of the type (II, M = Pt) are obtained on reduction of dichlorobis(triphenylphosphine)platinum in the presence of the appropriate acetylene[8,19]. Nickel complexes of this type (II, M = Ni) have also been reported[16]. The infra-red spectra of complexes (I) usually show a band at around 2000 cm^{-1}, assigned to the acetylenic C≡C stretching frequency, which has been reduced by about 250 cm^{-1} by comparison with that in the uncomplexed acetylene[18]. By contrast the platinum complexes (II, M = Pt) show this band at still lower frequencies; here the change in $\nu_{C\equiv C}$ on coordination is 400–575 cm^{-1} (Ref. 8, 19). This has been interpreted to mean that in (II) the acetylenic triple bond has been reduced nearly to a double bond and that the acetylene is now bonded to the metal by two σ-bonds, and is therefore assumed to be square planar and formally in the +2 oxidation state[8].

It has not been possible to prepare palladium complexes of type (I) as most acetylenes are very rapidly polymerized by palladium(II) compounds. It was there-

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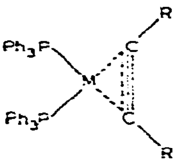
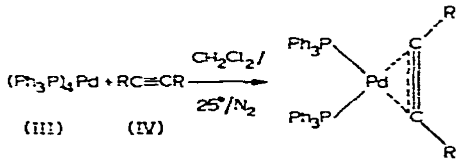


(II)



(Va, $R=CF_3$)
(Vb, R=COOMe)

fore of considerable interest to prepare complexes of the type (II, M = Pd) since their behaviour would shed light on the mechanism of the polymerization reactions. Attempts to prepare the palladium complexes (II, M = Pd) by the method used for the platinum compounds[19], namely hydrazine reduction of dichlorobis(triphenylphosphine)-palladium in the presence of the acetylene, were not successful. However, we found that two phosphines in tetrakis(triphenylphosphine)palladium(O)[21] (II) were readily replaced by acetylenes bearing strongly electron-withdrawing substituents.

An excess of hexafluoro-2-butyne (IV, $R = CF_3$) was passed into a methylene chloride solution of (III) under nitrogen. After thirty minutes methanol was added to the pale yellow solution and the methylene chloride removed on a rotary evaporator. The crude product was crystallized from methylene chloride–ether–methanol to give a 50% yield of (Va), m.p. 194–195°. [Found: C, 60.29; H, 3.76; F, 14.88; P, 7.82; mol. wt., 770. $C_{40}H_{30}F_6P_2Pd$ calcd.: C, 60.59; H, 3.81; F, 14.37; P, 7.81%; mol. wt. 793.] The complex (Vb) from dimethylacetylenedicarboxylate was prepared in 58% yield in a similar manner, m.p. 195–197°. [Found: C, 64.71; H, 4.87; P, 8.62; mol. wt., 763. $C_{40}H_{36}O_4P_2Pd$ calcd.: C, 65.25; H, 4.69; P, 8.01%; mol. wt. 773.]

The NMR spectra of (Va) and (Vb) were in agreement with their expected structures; the ^{19}F spectrum of (Va) showed a doublet centred at 10.7 ppm from benzotrifluoride (internal standard) due to coupling with ^{31}P (J_{P-F} 11.2 cps). (Vb) showed two resonances in the ^{1}H spectrum, one at 2.9 τ due to the phenyl protons and a sharp singlet at 6.8 τ due to the methoxycarbonyl group, with the expected intensity ratio of 5:1. The platinum analogue of (Vb), m.p. 188–190°, (I, M = Pt, R = COOMe), prepared by a similar route from tetrakis(triphenylphosphine)-platinum(O)[19] in 50% yield, showed the ^{1}H resonances at 2.9 τ (Ph) and 6.75 τ (Me). The infra-red spectra of (Va) and (I, M = Pt, $R = CF_3$) and also of (Vb) and (I, M = Pt, R = COOMe) respectively were nearly identical, showing the similarity of the structures of the palladium to the platinum complexes. The most marked differences were in the positions of the modified triple bond stretches. These are summarized in Table 1 with other values for comparison.

The table shows that considerable variation exists in $\nu_{C\equiv C}$ and hence in the bond order of this bond when coordinated to a metal. If it is also assumed that the lower the C≡C bond order the greater is the degree of sp^2 hybridization and hence the stronger the M–C bond, it is apparent that there is a continuous spectrum of bond-types between the very weak as in π-$C_5H_5Mn(CO)_2C_4F_6$ and the strong in the Pt and Ir complexes. Until an X-ray structure determination can give more accurate data on bonding, we have chosen to represent it by (II) and (V). The palladium complexes (V) are therefore expected to be intermediate in stability. This is born out by a comparison of the platinum and palladium complexes, thus (II, M = Pt, $R = CF_3$) is stable in solution while (Va) decomposes quite rapidly. Similarly (II, M = Pt,

TABLE I

TRIPLE BOND STRETCHING FREQUENCIES IN ACETYLENE COMPLEXES

Compound	$\nu_{C\equiv C}$ (*cm*$^{-1}$)	*Reference*
$CF_3C\equiv CCF_3$	2300 (Raman)	22
π-$C_5H_5Mn(CO)_2C_4F_6$	1919 (solution)	8
$(Ph_3P)_2RhCl\cdot C_4F_6$	1917 (mull)	14
$(Ph_3P)_2PdC_4F_6$ (Va)	1811, 1838 (solution)	—
$(\pi$-$C_5H_5)_2VC_4F_6$	1800	1
$(Ph_3P)_2PtC_4F_6$	1775 (solution)	8
$(Ph_3P)_2Ir(CO)Cl\cdot C_4F_6$	1773 (mull)	15
$(Ph_3P)_2Pd(C\cdot COOMe)_2$ (Vb)	1845 (1830 sh) (solution)	—
$(\pi$-$C_5H_5)_2V(C\cdot COOMe)_2$	1821	1
$(Ph_3P)_2Pt(C\cdot COOMe)_2$	1782 (1765 sh) (solution)	—

R = COOMe) is air-stable for sometime in the solid state while (Vb) slowly turns yellow on exposure to air. We have not, as yet, been able to prepare any complexes of the type (V, R = C_6H_5 or p-R'C_6H_5) by this method.

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