Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

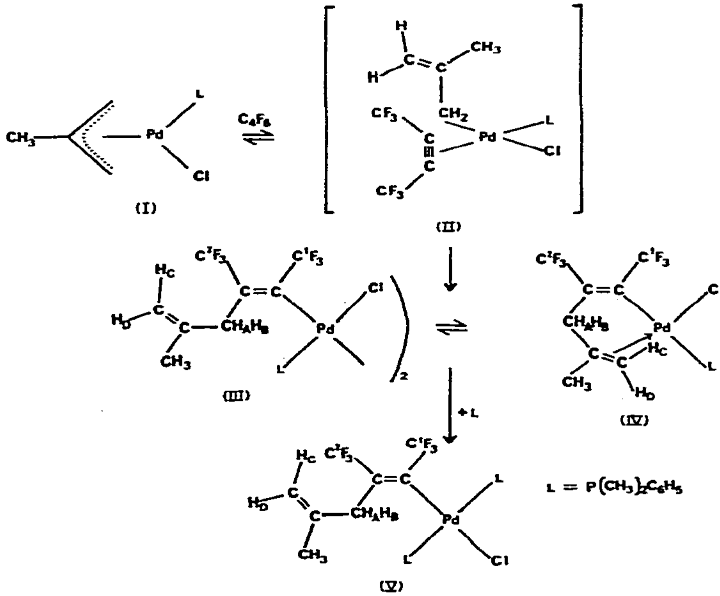
Insertion of hexafluoro-2-butyne into a palladium–allyl bond

T.G. APPLETON, H.C. CLARK*, R.C. POLLER and R.J. PUDDEPHATT
University of Western Ontario, London (Canada)

(Received March 7th, 1972)

Palladium–allyl bonds are reactive towards insertion by a variety of molecules, including carbon monoxide[1], isocyanides[2], dienes[3,4], and strained olefins[5–7]. However, no insertion of an acetylene into the palladium–allyl bond has been previously reported. Hexafluoro-2-butyne, $CF_3C{\equiv}CCF_3$, inserts quite readily into various metal–carbon bonds[8–10], and so might be expected to react with some palladium–allyl complexes.

Chloro(2-methallyl)(dimethylphenylphosphine)palladium(II), I[11], reacts over a period of several days at room temperature with excess hexafluorobutyne in a sealed pyrex tube in chloroform solution to form a complex with empirical formula corresponding to $PdCl(C_4H_7)(C_4F_6)[P(CH_3)_2(C_6H_5)]$.



---

*Author to whom correspondence should be addressed.

TABLE 1

NMR SPECTRA

Complex	*Solvent*	*Temperature*	*Chemical shifts* [a]			
			P–CH$_3$	*C–CH$_3$*	*H_AH_B*	*H_CH_D*
IV	CD_2Cl_2	–50°	NR	NR	3.4 (b)m	4.87 (b)s
III	CD_2Cl_2	–50	NR	NR		4.76 (b)s
III + IV	CD_2Cl_2	30	1.73 d	1.83 s	3.45 m	4.87 (b)s
V	$CDCl_3$	30	1.71 t 1.65 t	1.66 s	3.29 (b)s	4.79 (b)s

[a] For protons, ppm downfield from TMS. For fluorine, upfield from $CFCl_3$. (b) = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = complex multiplet, NR = Not resolved.
[b] ${}^2J(p\text{-H}) + {}^4J(p\text{-H})$. [c] Alternatively, ${}^4J(p\text{-}{}^1F) = 2.6$, ${}^5J(H_AH_B\text{–}{}^1F) < 1$.

The complex has an apparent molecular weight at 40° in chloroform of 660 (averaged over five solutions 0.005–0.03*M*). Over the rather narrow concentration range made available by instrument sensitivity and solubility of the complex, no concentration dependence greater than experimental error was noted. Comparison with molecular weights expected for monomeric and dimeric forms (497 and 994 respectively) suggests that a monomer–dimer equilibrium exists, with 49% of the complex as monomer. In benzene, the apparent molecular weight is 787, corresponding to 25% of the complex being monomer.

${}^1H$ and ${}^{19}F$ NMR spectra are consistent with an equilibrium between III and IV, their interconversion being rapid (on the NMR time-scale) at room temperature. At –50° separate signals corresponding to the two species are observed (Fig. 1(a)(b)). Details are given in Table 1 with labelling as in the scheme. The high value (14 Hz) of $J({}^1F\text{–}{}^2F)$ establishes the *cis*-geometryof the two $-CF_3$ groups about the double bond[12], so that *cis*-addition to the Pd–C bond has occurred as with olefins[5–7]. Several σ-C, π-olefin chelate structures analogous to that in IV are known[5–7,10,13]. In the solid state the complex probably exists as the dimer, III. No terminal Pd–Cl band is observed in its infrared spectrum near 300 cm^{-1}, but a band in its Raman spectrum at 261 cm^{-1} probably corresponds to a stretching mode involving the bridging chlorine atoms. Bands at 1650 (weak) and 1610 cm^{-1} probably correspond to the two distinct C=C stretching vibrations in the dimer. The stereochemistry about Pd of the monomer IV is not certain. The only evidence for that shown in the scheme (L *trans* to C) is the observation of P–Pd–C–${}^1F$ coupling (~6 Hz) in IV. The alternative isomer (Cl *trans* to C) would facilitate the III–IV interconversion.

Addition of another mole of phosphine causes formation of V. The phosphine-

		Resolved couplings (Hz)				
^1F	^2F	$^2J(p\text{-}CH_3)$	$J(^1F-^2F)$	$^4J(p\text{-}^1F)$	$^5J(H_AH_B-^1F)$	$^5J(p\text{-}^2F)$
49.92 q-d	58.10 q	NR	14	6	⩽2	<1
49.70 q-t	57.51 q	NR	14	<1	3	<1
49.86 q-d	58.77 (b)m	11.5	14.5	6.5	<2	NR
50.5 q-t	57.5 q-t	7.0 [b]	14.7	<1 [c]	2.6 [c]	7.1

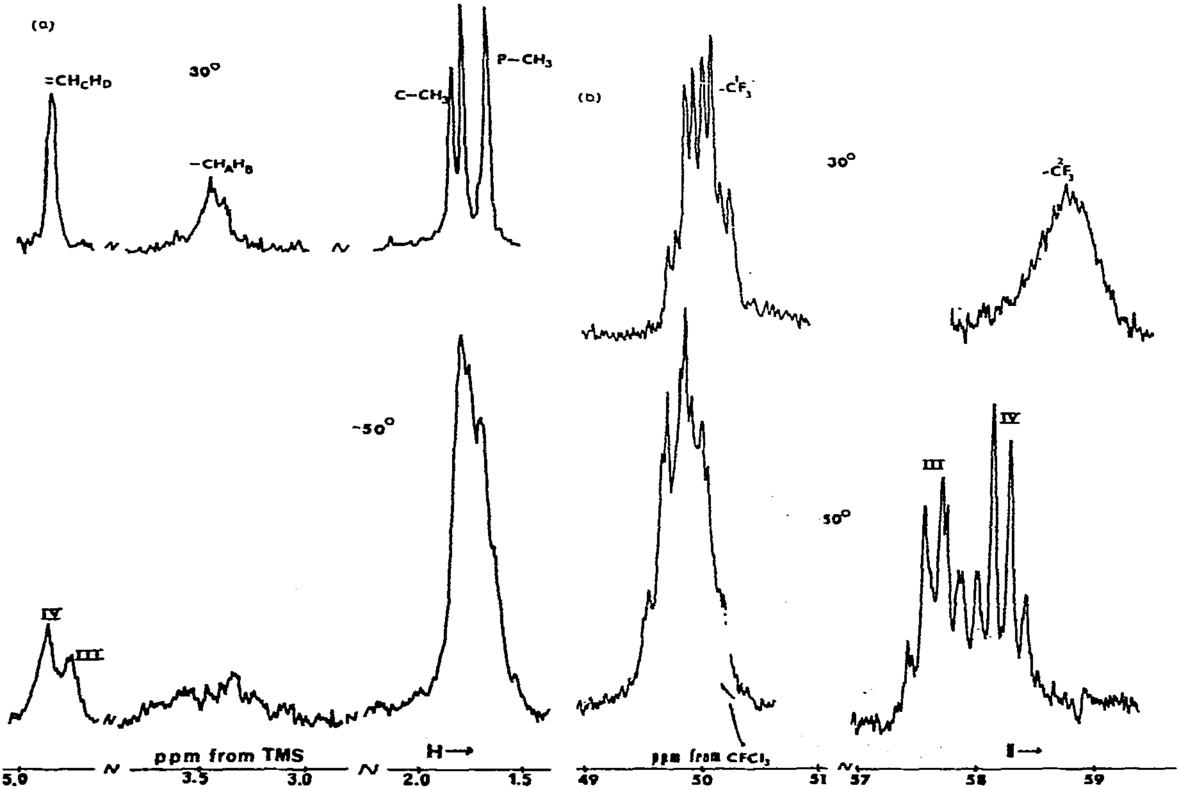


Fig. 1. (a) 100 MHz ^1H and (b) 94.1 MHz ^{19}F NMR spectra of $PdCl[C(CF_3)=C(CF_3)CH_2C(CH_3)=CH_2](PMe_2Ph)$ in CD_2Cl_2 at 30° and –50°.

methyl groups give overlapping 1/2/1 triplets in the proton NMR spectrum, indicating *trans*-phosphines[15]. The infrared spectrum of the solid shows bands at 1650, 1596 (ν(C=C)) and 305 (ν(Pd–Cl)) cm^{-1}.

Analogous reactions occur when L is triphenylphosphine, and when the 1-methallyl complex is used; insertion occurs, as usual[5], at the unsubstituted end of the allyl group. However, no reaction takes place under similar conditions between C_4F_6 and $(C_4H_7)PdCl_2Pd(C_4H_7)$, or between C_4F_6 and the hexafluoroacetylacetonate complex, $Pd(C_4H_7)(C_5HF_6O_2)$. The acetylacetonate complex, $Pd(C_4H_7)(C_5H_7O_2)$, caused polymerization of the acetylene, but no insertion products could be isolated. These reactivities may be rationalized if the insertion reaction proceeds via an intermediate such as II, which contains a σ-allyl group and a coordinated acetylene molecule. On the balance of its σ-basicity and π-acidity, C_4F_6, on the whole, tends to withdraw electrons from a metal ion to which it coordinates[16], so that the most stable palladium–acetylene bonds in complexes like II are formed when there is a high electron density on Pd (*i.e.* when a strong donor such as a phosphine is bound to palladium). This may be compared with the finding of Hughes and Powell that insertion of their relatively electron-rich olefins occurred most readily with the hexafluoroacetylacetonate complexes[3,5] (*i.e.* complexes in which the palladium is relatively positive, forming more stable intermediates with olefins which are overall electron donors), and the observation of Medema and Van Helden[4] that addition of a mole of triphenylphosphine blocks insertion of dienes into the palladium–allyl bond of π-allylpalladium halides and acetates.

REFERENCES

1 J. Tsuji and S. Osaka, *J. Amer. Chem. Soc.*, 87 (1965) 4075.
2 T. Kajimoto, H. Takahashi and J. Tsuji, *J. Organometal. Chem.*, 23 (1970) 275.
3 R.P. Hughes and J. Powell, *Chem. Commun.*, (1971) 275.
4 D. Medema and R. Van Helden, *Rec. Trav. Chim. Pays-Bas*, 90 (1971) 304, 326.
5 R.P. Hughes and J. Powell, *J. Organometal. Chem.*, 30 (1971) C45.
6 M.C. Gallazzi, T.L. Hanlon, G. Vitulli and L. Porri, *J. Organometal. Chem.*, 33 (1971) C45.
7 M. Zocchi, G. Tieghi and A. Albinati, *J. Organometal. Chem.*, 33 (1971) C47.
8 H.C. Clark and R.J. Puddephatt, *Inorg. Chem.*, 9 (1970) 2670.
9 H.C. Clark and R.J. Puddephatt, *Inorg. Chem.*, 10 (1971) 18.
10 A. Greco, M. Green and F.G.A. Stone, *J. Chem. Soc. A*, (1971) 3476.
11 P.W.N.M. Van Leeuwen, A.P. Praat and M. Van Diepen, *J. Organometal. Chem.*, 29 (1971) 433.
12 H.C. Clark and W.S. Tsang, *J. Amer. Chem. Soc.*, 89 (1967) 533.
13 T. Blackmore, M.I. Bruce, F.G.A. Stone, R.E. Davis and A. Garza, *Chem. Commun.*, (1971) 852.
14 D.M. Adams and A. Squire. *J. Chem. Soc. A*, (1970) 1808.
15 J.M. Jenkins and B.L. Shaw, *J. Chem. Soc. A*, (1966) 770.
16 T.G. Appleton, M.H. Chisholm and H.C. Clark, to be published.