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OXIDATIVE ADDITION OF IMIDOYL CHLORIDES TO TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0)

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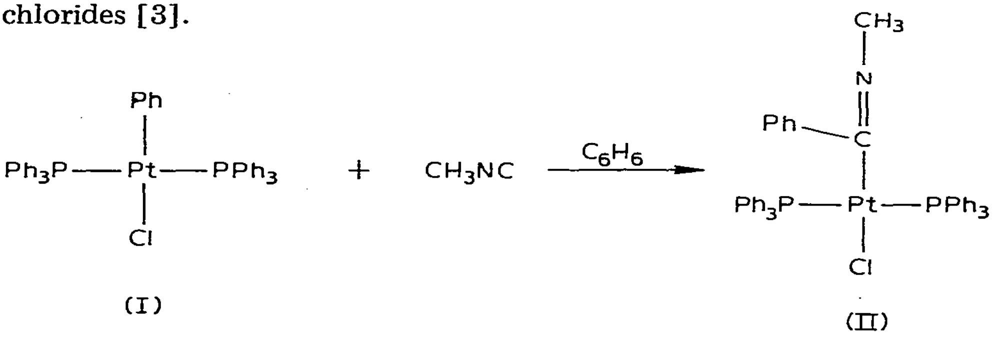
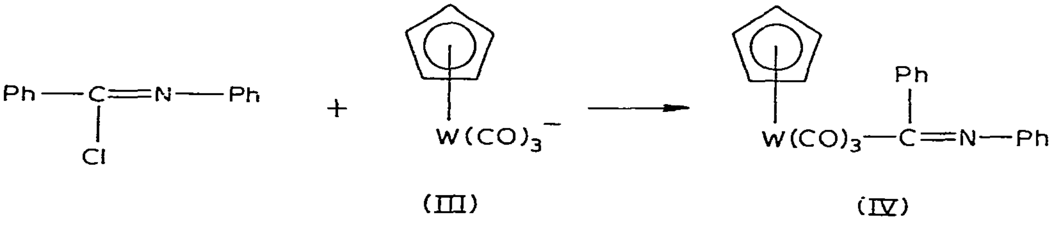
Summary

Reaction of a series of imidoyl chlorides with tetrakis(triphenylphosphine)palladium(0) at room temperature gives iminoacyl—palladium complexes in 55—91% yields. These square-planar complexes exist as the *trans*-isomer.

Introduction

Recently, there has been considerable interest in the synthesis of complexes containing iminoacyl ligands. The principal preparative methods for these complexes have involved nucleophilic addition or insertion reactions of isocyanide complexes [1, e.g. I→II], and halide displacement from imidoyl chlorides by metal carbonyl anions [2, e.g. III→IV]. Carbene rather than iminoacyl complexes were obtained from the reaction of rhodium(I) compounds with imidoyl chlorides [3].

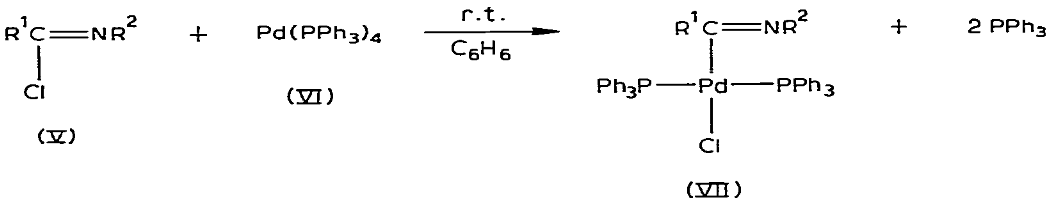




Vinylmetallic complexes are important as intermediates and catalysts in organic synthesis. Of particular note are coupling reactions involving palladium and copper complexes [4]. It seems reasonable to expect that complexes containing iminoacyl ligands should also have great synthetic potential in carbon—carbon bond forming reactions, with the possible subsequent manipulation of the imine function being an important feature. One obvious requirement in the development of new synthetic methodology using organometallic complexes is that the necessary organometallic intermediate be easily synthesized, in high yields, from readily available starting materials. We now report that oxidative addition of imidoyl chlorides to tetrakis(triphenylphosphine)palladium(0) affords iminoacyl—palladium complexes in good yield.

Results and discussion

Reaction of an imidoyl chloride (V) with tetrakis(triphenylphosphine)palladium(0) (VI), both readily accessible compounds, in benzene at room temperature afford *trans* square-planar iminoacyl—palladium complexes, VII. The yields of analytically pure products usually were excellent (Table 1), and structure identification was made on the basis of analytical and spectral results (Table 2). The iminoacyl complex VII, $R^1 = R^2 = Ph$, has been isolated previously from the reaction of triphenylphosphine with $[Pd(PPh_3)C(=NPh)PhCl]_2$, the latter in turn being obtained from an isocyanide complex [5].



R^1 = 2-furyl ; R^2 = p-$CH_3OC_6H_4$
R^1 = Ph ; R^2 = Ph , p-ClC_6H_4 , p-$CH_3C_6H_4$
R^1 = p-BrC_6H_4 ; R^2 = Ph
R^1 = p-$CH_3OC_6H_4$; R^2 = Ph

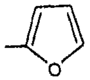
All of the iminoacyl complexes melt with decomposition, the decomposition point being significantly higher when the melting point determination was carried out in a nitrogen atmosphere than in air (Table 1).

The carbon—nitrogen stretching adsorption for VII occurs in the infrared spectra at lower frequency (1559—1571 cm^{-1}) when compared to the corresponding imidoyl chloride [6]. Proton and phosphorus-31 magnetic resonance spectra of the iminoacyl complexes also support the assigned structure, with the single ^{31}P resonance at δ 21.12—21.48 indicative of a *trans*-geometry for the square-planar complex [7].

We are actively investigating the applications of iminoacylpalladium complexes in organic synthesis.

TABLE 1

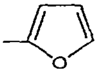
YIELD AND ANALYTICAL DATA FOR THE IMINOACYL—PALLADIUM COMPLEXES (VII)

VII, R^1 =, R^2 =	Colour	Yield [a] (%)	M.p. (°C) under		Anal. Found (Calcd.) (%)		
			N_2	air	C	H	N
Ph, Ph	Yellow	81	253.5	216 [b]	69.71(69.51)	4.62(4.76)	4.27(4.46)
Ph, p-ClC_6H_4	Yellow	77	245	197	66.90(66.80)	4.27(4.46)	1.78(1.59)
p-BrC_6H_4, Ph	Yellow	55	229	208	63.59(63.59)	4.53(4.25)	2.00(1.51)
p-$CH_3OC_6H_4$, Ph	Pale yellow	85	230.4—231.6	194	68.23(68.50)	5.20(4.83)	2.08(1.60)
Ph, p-$CH_3C_6H_4$	Green-yellow	91	257.6—259.4	218	69.45(69.78)	4.92(4.92)	2.19(1.63)
 , p-$CH_3OC_6H_4$	Pale yellow	86	231.6—234.0	204.5—207.5	66.37(66.52)	4.39(4.65)	1.94(1.62)

[a] Yields are of analytically pure products, and are based on reactant $Pd(PPh_3)_4$. [b] lit m.p. 215°C dec. [5].

TABLE 2

PERTINENT SPECTRAL DATA FOR VII

VII, R^1=, R^2=	IR, ν_{CN} [a] (cm^{-1})	^1H NMR, δ [b] (ppm)	^{31}P NMR, δ [c] (ppm)
Ph, Ph	1566		21.12
Ph, p-ClC_6H_4	1564	6.78—7.95(m)	21.48
p-BrC_6H_4, Ph	1565	6.80—7.80(m)	21.44
p-$CH_3OC_6H_4$, Ph	1562	3.77(s, 3H) 6.40—8.00(m, 39 H)	21.46
p-Ph, p-$CH_3C_6H_4$	1571	2.46(s, 3 H) 7.00—8.10(m, 39 H)	21.35
 , p-$CH_3OC_6H_4$	1559	3.90(s, 3 H), 6.10, 6.66, 6.83, 7.17—7.80(m, 37 H)	21.44

[a] Nujol mull. [b] $CDCl_3$ with tetramethylsilane as internal standard. [c] In $CDCl_3$ with 85% H_3PO_4 as external standard.

Experimental

General

Melting points were recorded on a Gallenkamp apparatus, and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona, and by Butterworths Microanalytical Consulting Ltd., Teddington, Great Britain. Infrared spectra were recorded on a Unicam SP1100 spectrometer, equipped with a calibration standard. A Varian T-60 spectrometer was used for proton magnetic resonance measurements, and phosphorus-31 spectra were recorded on a Varian FT-80 spectrometer.

Tetrakis(triphenylphosphine)palladium was prepared according to the method described by Coulson [8], and was recrystallized from benzene in the presence of triphenylphosphine [9]. The imidoyl chlorides (V) were prepared by literature methods [10,11]. Solvents were purified by standard methods. All reactions were run under an atmosphere of dry nitrogen.

Reaction of imidoyl chlorides (V) with $(Ph_3P)_4Pd$ (VI)

To a benzene solution (15—20 ml) of tetrakis(triphenylphosphine)palladium (0.54—0.63 mmol) were added two equivalents of an imidoyl chloride. The reaction mixture was stirred at room temperature for 15—20 h, concentrated in vacuo, and the residue obtained was triturated with diethyl ether to remove any triphenylphosphine. The crude product then was purified in each case, as follows:

VII, R^1 = R^2 = Ph. Recrystallization from 20 ml of dichloromethane/hexane (1/3) gave yellow micro-crystals of analytically pure complex.

VII, R^1 = Ph, R^2 = p-ClC_6H_4. The powder was chromatographed on silica gel. Elution with dichloromethane/ether (1/1) gave reasonably pure VII. Analytically pure material was obtained by washing VII twice with diethyl ether (10 ml portions), then dissolving the complex in CH_2Cl_2 (3 ml), and adding hexane until the solution became cloudy.

VII, R^1 = p-BrC_6H_4, R^2 = Ph. The crude material was dissolved in CH_2Cl_2

(5 ml) and reprecipitated with diethyl ether (10 ml). The solid was filtered and recrystallized three times from CH_2Cl_2/hexane (1/2) to give bright yellow plates.

VII, $R^1 = p\text{-}CH_3OC_6H_4$, $R^2 = Ph$. Leaflets were obtained on recrystallization of the crude product twice from 10—15 ml of CH_2Cl_2/hexane (1/2).

VII, $R^1 = Ph$, $R^2 = p\text{-}CH_3C_6H_4$. The crude product was triturated with ether, and then recrystallized from 25 ml of CH_2Cl_2/hexane (1/3).

VII, R^1 = *2-furyl*, $R^2 = p\text{-}CH_3OC_6H_4$. The complex was dissolved in CH_2Cl_2 (2 ml), reprecipitated with diethyl ether, filtered, and washed with diethyl ether. This treatment was repeated several times, and then the solid was dissolved in benzene (5 ml). Filtration followed by addition of hexane to the filtrate gave analytically pure complex.

Acknowledgements

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References

1 For an excellent review of isocyanide complexes, see P.M. Treichel, Adv. Organometal. Chem., 11 (1973) 21.
2 R.D. Adams, D.F. Chodosh and N.M. Golembeski, J. Organometal. Chem., 139 (1977) C39.
3 P.B. Hitchcock, M.F. Lappert, G.M. McLaughlin and A.J. Oliver, J. Chem. Soc. Dalton, (1974) 68.
4 R. Noyori, in H. Alper (Ed.), Transition Metal Organometallics in Organic Synthesis, Vol. I, pp. 83—187.
5 B. Crociani, M. Nicolini and T. Boschi, J. Organometal. Chem. 33 (1971) C81.
6 H. Ulrich, The Chemistry of Imidoyl Halides, Plenum Press, New York, 1968.
7 P.E. Garrou and G.E. Hartwell, J. Organometal. Chem., 71 (1974) 443, and references cited therein.
8 D.R. Coulson, Inorg. Syn., 13 (1972) 121.
9 N. Takahashi, K. Sonogashira and N. Hagihara, Nippon Kagaku Zasshi, 87 (1966) 610; Chem. Abstr., 65 (1966) 14485.
10 V. Hahn and M. Grdinic, J. Chem. Eng. Data, 11 (1966) 211.
11 J.V. Braun and W. Pinkernelle, Ber., 67 (1934) 1218.