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Preparation of cationic (keto-stabilized phosphonium or sulphonium ylide)(η^5-cyclopentadienyl)(triphenylphosphine)palladium(II) complexes

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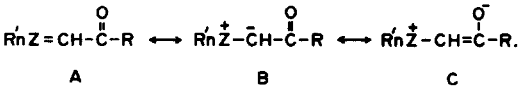
Abstract—In the presence of $AgClO_4$, chloro(η^5-cyclopentadienyl)(triphenylphosphine)palladium(II) was treated with triphenylphosphonium benzoylmethylide triphenylphosphonium acetylmethylide, and dimethylsulphonium benzoylmethylide to yield the corresponding ylide complexes, [Pd(η^5-cyclopentadienyl)(ylide)(triphenylphosphine)]ClO_4 with ylidic carbon-metal σ bonds. When $NaClO_4$ was used in place of $AgClO_4$, the ylide complexes were not obtained.

Some keto-stabilized phosphonium and sulphonium ylides exhibit well-known interaction[1,2] with various electrophiles through the nucleophilic ylidic carbon next to onium atoms. The nucleophilic ylides displaced labile ligands in $[PdCl_2(SR_2)_2]^3$, $[Pd_2Cl_4(CH_2{=}CHPh)_2]^{4,5}$, and $[PdCl_2(NCR)_2]^{4,5}$, and cleaved chloro-bridges in $[Pd_2Cl_4(PR_3)_2]^6$ to give stable ylide complexes with ylidic carbon–palladium σ bonds. However, no attempt seems to have been described on the reaction of the ylides with (η^5-cyclopentadienyl)halo(tertiary phosphine)palladium(II) compounds. This note deals with the reaction of some ylides with chloro(η^5-cyclopentadienyl)(triphenylphosphine)palladium(II) (I) in the presence of silver perchlorate. Recently Kurosawa[7] reported that a bromo analogue of 1 was treated with silver perchlorate in the presence of olefins or carbon monoxide to replace bromine with these incoming ligands and to yield respective cationic complexes retaining the η^5-cyclopentadienyl moiety.



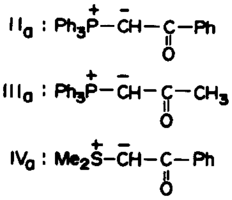
$$R'_nZ{=}CH{-}\overset{O}{\overset{\|}{C}}{-}R \longleftrightarrow R'_n\overset{+}{Z}{-}\overset{-}{C}H{-}\overset{O}{\overset{\|}{C}}{-}R \longleftrightarrow R'_n\overset{+}{Z}{-}CH{=}\overset{O^-}{\overset{|}{C}}{-}R.$$

A B C

RESULTS AND DISCUSSION

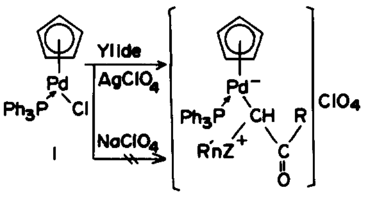
(η^5-Cyclopentadienyl)palladium complex I was prepared in a very low yield from the reaction of thallium cyclopentadienide with a halogen-bridged complex $[Pd_2Cl_4(PPh_3)_2]$, owing to the low solubility of the reactants, as described by Cross and Wardle[8]. However, sodium cyclopentadienide is soluble in THF and reacted readily with $[Pd_2Cl_4(PPh_3)_2]$ to afford I in a high yield.

Complex I was treated with some keto-stabilized phosphonium and sulphonium ylides, which included triphenylphosphonium benzoylmethylide (II_a), triphenylphosphonium acetylmethylide (III_a), and dimethylsulphonium benzoylmethylide (IV_a). These ylides could not displace chlorine coordinated to palladium in the presence of sodium perchlorate, implying low nucleophilicity of these ylides and fair stability of the palladium-chlorine bond. On the other hand, silver perchlorate, a strong halogen-trapping reagent could remove the chlorine from palladium, leading to the coordination of the ylides to palladium. Actually, the ylides II_a, III_a, and IV_a formed stable η^5-cyclopentadienyl ylide complexes $[Pd(\eta^5\text{-}C_5H_5)(PPh_3)\{CH(COR)ZR'_n\}]ClO_4$ ($ZR'_n = PPh_3$, $R = Ph$, II_b; $ZR'_n = PPh_3$, $R = Me$, III_b; $ZR'_n = SMe_2$, $R = Ph$, IV_b), respectively, as shown in Tables 1 and 2.



$$II_a : Ph_3\overset{+}{P}{-}\overset{-}{C}H{-}\underset{O}{\underset{\|}{C}}{-}Ph$$
$$III_a : Ph_3\overset{+}{P}{-}\overset{-}{C}H{-}\underset{O}{\underset{\|}{C}}{-}CH_3$$
$$IV_a : Me_2\overset{+}{S}{-}\overset{-}{C}H{-}\underset{O}{\underset{\|}{C}}{-}Ph$$

These ylide complexes exhibited a $\nu(C=O)$ band in the range of 1620 to 1640 cm^{-1}, and the shift of the bands towards higher



II_b, III_b, IV_b

Table 1. Yields and properties of the palladium complexes

Complex	Yield[b) %]	Mp[d)] °C	Color	Found(Calcd), % C	H
I	80[c)]	136-138	Dark green	59.03(58.87)	4.40(4.30)
II_b[a)]	22	127-131	Yellowish green	62.45(62.18)	4.48(4.42)
III_b	25	151-162	Pale green	62.20(62.06)	4.75(4.62)
IV_b	9	113-133	Brown	55.45(55.55)	4.61(4.52)

a) Isolated as a hemisolvate of CH_2Cl_2. b) Based on I, unless noted elsewhere. c) Based on $Pd_2Cl_4(PPh_3)_2$. d) With decomposition.

Table 2. Spectroscopic properties of free ylides and their palladium complexes

	^{1}H-NMR$^{a)}$, δ Value from TMS			IR$^{d)}$, cm^{-1}	
	δ (CH)	δ (CH$_3$)	δ (Cp)$^{b)}$	ν(C=O)	ν(Cl-O)
I			5.48(d,3.0)		
II$_a$	4.57(d,24.3)$^{c)}$			1524	
II$_b$	4.25(ad,4.0)		5.00(d,2.0)	1620	1090
III$_a$	3.69(d,27.0)$^{c)}$	2.08(d,1.8)$^{c)}$		1530	
III$_b$	3.07(ad,1.1)	2.01(ad, 2.2)	5.19(d,2.2)	1640	1090
IV$_a$	4.29(s)	2.91(s)		1515	
IV$_b$	4.10(d,6.00)$^{b)}$	2.77(s), 2.69(s)	5.37(d,2.2)	1620	1085

a) In CDCl$_3$. Signal shape and coupling constant are given in the parentheses. Abbreviations used : s=singlet, d=doublet, ad=apparent doublet. b) Coupled with ^{31}P in triphenylphosphine. c) Coupled with onium ^{31}P nucleus. d) In KBr disk.

wave numbers upon coordination indicates larger contribution of the canonical structure B and smaller one of C, compared with those in free ylides. These results and the lack of an enolate C⋯O stretching band[9] suggest that the bonding mode of the ylides to palladium is through the ylidic carbon rather than through an enolate oxygen. Similar high-wavenumber shifts were observed in some keto-stabilized ylide complexes[3–6] upon coordination through the nucleophilic carbon. The chemical shifts of the ylide methine protons of these cationic complexes are at comparatively higher fields than those of free ylides and of reported neutral palladium ylide complexes[4–6]. The high-field resonances in the present complexes are possibly attributed to the electron donation to palladium from triphenylphosphine and η^5-cyclopentadienyl groups. Saito *et al.*[10] noticed similar highfield resonances of the methine protons in cationic ylide complexes. It is noteworthy that magnetic non-equivalence of two methyl groups on sulfur in **IV**$_b$ was observed, due to the presence of the neighboring dissymmetric carbon which was induced by the σ-bond formation between the carbon and the palladium atoms.

In sharp contrast to the cases of **II**$_a$, **III**$_a$, and **IV**$_a$, analogous cyclopentadienyl ylide complexes were not isolated from triphenylphosphonium methoxycarbonylmethylide (**V***a*) and dimethylsulphonium diacetylmethylide (**VI**$_a$). ^{1}H NMR spectra of unidentified products from **V**$_a$ and **VI**$_a$ suggested loss of the cyclopentadienyl group.

EXPERIMENTAL

General procedures. IR and ^{1}H NMR spectra and melting points were measured according to the methods described in the previous paper.[11] Ylide compounds were prepared by the literature methods.[1,2]

Preparation of chloro(η^5-cyclopentadienyl)(triphenylphosphine)palladium(II) **I**. Complex **I** was prepared essentialy by the method described by Cross and Wardle[8], except that sodium cyclopentadienide was used in place of the thallium salt at temperatures lower than 0°C.

Reaction of phosphonium or sulphonium ylides with **I** *in the presence of AgClO$_4$.* To a mixture of triphenylphosphonium benzoylmethylide and **I** in THF, an equivalent quantity of AgClO$_4$ in benzene was added slowly. The precipitates formed were collected and recrystallized from dichloromethane, diethyl ether, and *n*-hexane to afford yellowish green powder of η^5-cyclopentadienyl)(triphenylphosphonium benzoylmethylide)(triphenylphosphine)palladium(II) perchlorate **II**$_b$. (η^5-Cyclopentadienyl)(triphenylphosphonium acetylmethylide)(triphenylphosphine)palladium(II) perchlorate **III**$_b$ and (η^5-cyclopentadienyl)(dimethylsulphonium benzoylmethylide)(triphenylphosphine)palladium(II) perchlorate **IV**$_b$ were prepared similarly.

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