

Synthesis, characterization, and spectroscopic studies of palladium(II) and silver(I) complexes of 4-methoxybenzoylmethylenetriphenylphosphorane and 4-fluorobenzoylmethylenetriphenylphosphorane

Kazem Karami

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Abstract The reactions of 4-methoxybenzoylmethylenetriphenylphosphorane ylide (MOBPPY), $\{(\text{Ph})_3\text{PCHCOC}_6\text{H}_4\text{OMe}\}$, and 4-fluorobenzoylmethylenetriphenylphosphorane ylide (FBPPY) with $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2\text{-}\kappa^2\text{-C-N})\text{CIL}]$ ($\text{L} = \text{Py}$, 3-MePy, 4-MePy, or PPh_3), in equimolar ratios in CH_2Cl_2 yield $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2\text{-}\kappa^2\text{-C-N})\text{L}(\text{Ye})]\text{TfO}$ [$\text{L} = \text{PPh}_3$, $\text{Ye} = \text{MOBPPY}$; $\text{L} = \text{PPh}_3$, $\text{Ye} = \text{FBPPY}$; $\text{L} = \text{Py}$, $\text{Ye} = \text{MOBPPY}$; or $\text{L} = 3\text{-MePy}$, $\text{Ye} = \text{MOBPPY}$]. The reaction of MOBPPY with AgOTf ($\text{OTf} = \text{CF}_3\text{SO}_3$) in molar ratios (2:1) using dry acetone as solvent gives $[\text{Ag}(\text{MOBPPY})_2]\text{OTf}$.

Introduction

The α -ketostabilized phosphorus ylides $\text{Ph}_3\text{PCH}=\text{C}(\text{H})\text{COR}$ ($\text{R} = \text{Me}$, Ph , OMe) are interesting ligands in organometallic chemistry and useful intermediates for organic synthesis [1–4]. Carbonyl-stabilized phosphorus ylides are interesting ligands because they can behave as C- or O-donors owing to the delocalization of the ylidic electron pair [5]. This delocalization also makes these ligands weak nucleophiles, but this does not reduce their interest as ligands; indeed it was their weak donor ability that allowed other groups to prepare new types of ylide complexes [5, 6]. This ambidentate character facilitates the preparation of stable metal complexes (Scheme 1) in which the ylide can be O- (both *cisoid* and *transoid* forms, b) [6] or C-coordinated (a) [7].

In the compounds reported to date, the chemical behavior of the α -ketostabilized phosphorus ylides has been clearly dominated by the C-coordinated form [7–11], and very few examples of O-coordinated ylides are known [6, 12–15]. Some of these examples contain the ylide O-coordinated to a hard, very exophilic metal center, as $\text{Sn}(\text{IV})$ [12] or group 4 metals in high oxidation number [13]. Other attempts to obtain this kind of coordination to soft metals such as $\text{Pd}(\text{II})$, $\text{Pt}(\text{II})$, and $\text{Hg}(\text{II})$ gave C-coordination [16]. I Synthesis Pd Complexes (1)–(4) made by reaction of stabilized phosphorus ylides (MOBPPY and FBPPY) with $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2\text{-}\kappa^2\text{-C,N})\text{LCl}]$ ($\text{L} = \text{Py}$, 3-MePy, 4-MePy, or PPh_3) and AgOTf or TiOTf in this article. I have also synthesized a cationic complex (5) of 4-methoxybenzoylmethylenetriphenylphosphorane with AgOTf containing the C-bound ylide.

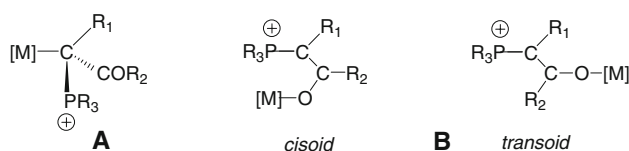
Experimental

Diethyl ether was distilled over a mixture of sodium and benzophenone just before use [16]. All other solvents were reagent grade and used without further purifications. Solution-state ^1H and ^{31}P NMR spectra at 300 K were obtained in CDCl_3 using a 500 MHz Bruker spectrometer operating at 500.13 MHz for ^1H and 161.97 MHz for ^{31}P and referenced to H_3PO_4 (85%) for $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. IR spectra were recorded on a FT-IR JASCO 680 spectrophotometer, and the measurements were made by the KBr disk method. Melting points were measured on a Gallenamp 9B 3707 F apparatus.

Materials

All chemicals were purchased from Merck. The ylides were synthesized by the reaction of triphenylphosphine with a

K. Karami (✉)
Department of Chemistry, Isfahan University of Technology,
Isfahan 84156/83111, I.R. Iran
e-mail: karami@cc.iut.ac.ir



Scheme 1 R1 = H, R2 = C₆H₄-O-Me or C₆H₄-F

chloroform solution of 2-bromo-4-methoxyacetophenone or 2-bromo-4-fluoroacetophenone and dehydrogenated with NaOH [17, 18]. All solvents were dried by the reported methods [19].

Preparation of complexes (1)–(4)

To a solution of [Pd(C₆H₄CH₂NH₂-κ²-C-N)(L)Cl] (0.13–0.22 mmol) in THF or CH₂Cl₂ plus CH₃COCH₃ (1:3), solid TlTfO (0.13–0.22 mmol) was added. The resulting suspension was stirred for 2 h at RT and filtered through a plug of celite or plug of MgSO₄. To the freshly obtained solution, cooled at 0 °C, MOBPPY or FBPPY (0.13–0.22 mmol) was added. After 1–3 h of stirring at 0 °C, the crude complex had precipitated as a white solid. This was soluble in CH₂Cl₂ at room temperature. The solvent was completely removed and Et₂O (30 mL) added to give a white powder, which was filtered off, air dried, and washed with Et₂O to give complexes (1)–(4), which were recrystallized from CH₂Cl₂-*n*-hexane for NMR measurements. The complexes are readily soluble in CH₂Cl₂, acetone, and CHCl₃ but insoluble in Et₂O and *n*-hexane.

Complex [Pd(C₆H₄CH₂NH₂-κ²-C-N)PPh₃MOBPPY]OTf (1)

Yield: 53%; Color: white; Mp: 137 °C; IR (cm⁻¹): ν(N-H) = 3332–3256, ν(C=O) = 1475; ¹HNMR: (500 MHz, CDCl₃, RT): δ (ppm) 7.84–7.09 (m, 34H, 6C₆H₅, C₆H₄), 6.85 (d, 3H, C₆H₄), 6.31 (br, 1H, C₆H₄), 4.3 (d, 1H, CH ylide, ²J_{PH} = 25 Hz), 3.86 (s, 3H, OMe), 3.2 (s, 2H, NH₂), 1.70 (s, 2H, CH₂ N); ³¹PNMR: (500 MHz, CDCl₃, RT): δ (ppm) 40.93 (s, Ph₃P-Pd), 14.06 (s, P⁺Ph₃). Elemental analysis: Calc: C, 61.6; H, 4.5; N, 1.4; S, 3.1; Found: C, 62.0; H, 4.4; N, 1.5; S, 3.4; Λ = 126 Ω⁻¹ mol⁻¹ cm².

Complex [Pd(C₆H₄CH₂NH₂-κ²-C-N)PPh₃FBPPY]OTf (2)

Yield: 76%; Color: white; Mp: 149 °C; IR (cm⁻¹): ν(N-H) = 3302–3256, ν(C=O) = 1475; ¹HNMR: (500 MHz, CDCl₃, RT): δ (ppm) 8.16–6.91 (m, 34H, 6C₆H₅, C₆H₄), 6.9 (d, 2H, C₆H₄), 6.40 (br, 2H, C₆H₄), 4.4 (d, 1H, CH ylide, ²J_{PH} = 25 Hz), 3.4 (s, 2H, NH₂), 1.73 (s, 2H, CH₂ N); ³¹PNMR: (500 MHz, CDCl₃, RT): δ (ppm) 41.28

(s, Ph₃P-Pd), 13.68 (s, P⁺Ph₃). Elemental analysis: Calc: C, 61.80; H, 4.2; N, 1.40; S, 3.1; Found: C, 62.00; H, 4.6; N, 1.8; S, 3.2; Λ = 126 Ω⁻¹ mol⁻¹ cm².

Complex [Pd(C₆H₄CH₂NH₂-κ²-C-N)(Py)(OC(MeO-4-C₆H₄)=CHPPh₃)]OTf (3)

Yield: 48%; Color: white; Mp: 178 °C; IR (cm⁻¹): ν(N-H) 3306–3244, ν(C=N) py 1604, ν(C=O)1486; ¹HNMR: (500 MHz, CDCl₃, RT): δ (ppm) 8.33 (br, 2H, Py), 8.02 (br, 2H, Py), 7.8–7.26 (m, 19H, 3C₆H₅ + C₆H₄), 7.33 (br, 1H, Py), 6.95 (d, 2H, C₆H₄, ³J_{H-H} = 6.97 Hz), 6.89(s br, 1H, C₆H₄), 6.71 (t br, 2H, NH₂), 5.96 (s, 1H, C₆H₄), 4.5 (d, 1H, CH ylide, ²J_{P-H} = 23.9 Hz), 4 (br, 2H, CH₂ N), 3.87 (s, 3H, OMe); ³¹PNMR: (500 MHz, CDCl₃, RT): δ (ppm) 16.0 (s, P⁺Ph₃). Elemental analysis: Calc: C, 56.49; H, 4.26; N, 3.30; S, 3.77; Found: C, 56.89; H, 4.30; N, 3.81; S, 3.85; Λ = 175 Ω⁻¹ mol⁻¹ cm².

Complex [Pd(C₆H₄CH₂NH₂-κ²-C,N)(3-Me-Py)(OC(MeO-4-C₆H₄)=CHPPh₃)]OTf (4)

Yield: 62%; Color: white; Mp: 178 °C; IR (cm⁻¹): ν(N-H) 3306–3244, ν(C=N) py 1604, ν(C=O) 1492; ¹HNMR: (500 MHz, CDCl₃, RT): δ (ppm) 8.02 (br, 1H, Py), 8.02 (d, 2H, Py, ³J_{H-H} = 7.56 Hz), 7.8–7.26 (m, 15H, 3C₆H₅), 7.18 (br, 1H, Py), 6.95 (d, 2H, C₆H₄, ³J_{H-H} = 8.2 Hz), 6.89 (s br, 1H, C₆H₄), 6.73 (s br, 1H, C₆H₄), 5.96 (s br, 1H, C₆H₄), 4.4 (d, 1H, CH ylide, ²J_{P-H} = 23.2 Hz), 4.04 (br, 2H, NH₂), 3.87 (s, 3H, OMe), 2.27 (s br, 3H, Me-Py), 1.78 (s br, 2H, CH₂N); ³¹PNMR: (500 MHz, CDCl₃, RT): δ (ppm) 16.2 (s, P⁺Ph₃). Elemental analysis: Calc: C, 57.0; H, 4.2; N, 3.4; S, 3.9; Found: C, 56.9; H, 4.30; N, 3.8; S, 3.8; Λ = 148 Ω⁻¹ mol⁻¹ cm².

Preparation of [Ag(MOBPPY)₂]CF₃SO₃ (5)

MOBPPY (0.410 g, 1 mmol) was added to a solution of AgOTf (0.256 g, 1 mmol) in acetone (10 mL). The solution was stirred protected from the light for 1 h and then filtered through MgSO₄. The volume of solvent was reduced under vacuum to about 2 mL. Diethyl ether (25 mL) was added to precipitate [Ag{CH(PPh₃)-C(O)C₆H₄-OMe}TfO] (5) as a white powder. Mp: 176 °C; ¹HNMR: (500 MHz, CDCl₃, RT): δ (ppm) 8.06 (d, 2H, 2H_o, C₆H₄, ³J_{H-H} = 8.5 Hz), 7.56–7.30 (m, 15H, 3C₆H₅), 6.81 (d, 2H, 2H_m, C₆H₄, ³J_{H-H} = 8.8 Hz), 5.22 (br s, 1H, CHP), 3.86 s, 3H, OMe); ³¹PNMR: (500 MHz, CDCl₃, RT): δ (ppm) 24.75 (s, P⁺Ph₃). Anal. Calc for C₅₅H₄₆AgF₃O₇P₂S: C, 61.3; H, 4.3; S, 3.0. Anal. Found: C, 61.5; H, 3.9; S, 3.1; Λ = 72 Ω⁻¹ mol⁻¹ cm².

Results and discussion

Synthesis

MOBPPY and FBPPY were prepared following the method reported by Ramirez et al. in two steps [18]. The reaction of 2-bromo-4'-methoxyacetophenone and 2-bromo-4'-fluoroacetophenone with PPh_3 gives the phosphonium salts, which react with a weak base in H_2O , allowing the isolation of ylides FBPPY and MOBPPY as compounds stable to air and moisture.

When a freshly prepared solution of $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2-\kappa^2\text{-C-N})\text{L}(\text{S})]\text{TfO}$ was reacted with MOBPPY or FBPPY (1:1 molar ratio) in THF or Me_2CO at 0°C , white solids of stoichiometry $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2-\kappa^2\text{-C-N})\text{L}(\text{Ye})]\text{TfO}$ (1)–(4) (Ye = MOBPPY or FBPPY) precipitated in good yields after 30 min of stirring (Scheme 2).

Spectroscopy

The $\nu(\text{CO})$ band, which is sensitive to complexation, occurs at 1504 and 1516 cm^{-1} in the parent ylides (Table 1), as in the case of other resonance stabilized ylides [21]. In general, coordination of the ylide through C causes an increase in $\nu(\text{CO})$ while for O-coordination a lowering of $\nu(\text{CO})$ is expected. The IR absorption bands observed for these complexes show a lowering of $\nu(\text{CO})$, indicating coordination of the ylide oxygen for the Pd complexes (1)–(4). The IR spectrum of (5) shows a strong absorption at 1612 cm^{-1} , which is shifted to higher frequency with respect to the starting ylide FBPPY (1516 cm^{-1}), meaning that the ylide

is C-bonded to the Ag center. The $\nu(\text{P}^+-\text{C}^-)$ band which is also diagnostic of the coordination occurs at 837 cm^{-1} in $(\text{C}_6\text{H}_5)_3\text{P}^+-\text{CH}_2\text{COC}_6\text{H}_4\text{-O-Me}$ (phosphonium salt) and at 855 cm^{-1} in $(\text{C}_6\text{H}_5)_3\text{PCHCOC}_6\text{H}_4\text{-O-Me}$. In the present study, the $\nu(\text{P}^+-\text{C}^-)$ values for all five complexes were shifted to lower frequency (Table 1), suggesting some removal of electron density from the P–C bond. The $^1\text{HNMR}$ spectra of complexes (1)–(4) show a doublet or broad signal attributed to the proton methine CH at 4.3–4.5 ppm with $^2J_{(\text{PH})} = 25\text{ Hz}$ (1); these values are close to those observed in other O-bound complexes [6, 12–15].

The $^1\text{HNMR}$ spectra of complexes (1)–(4) showed only one signal for the CH methine with a coupling constant $^2J_{\text{P-H}}$ near to that of the free ylides and close to those observed in other O-bonded complexes; this coupling is usually smaller in C-linked ylides [7–11]. The $^1\text{HNMR}$ of complex (5) show one broad signal for CH methine. The signal due to the methine proton, when recorded in CDCl_3 , was broad for complexes (1)–(4). This indicates probably that the ylide dissociates in solution [19]. The $^1\text{HNMR}$ spectra of complexes (1)–(4) show a doublet or broad signal attributed to the methine proton CH at 4.3–4.5 ppm., with $^2J_{(\text{PH})} = 25\text{ Hz}$ (1); these values are close to those observed in other O-bound complexes. Complex (5) wherein the ylide is C-coordinated exhibits a $^2J_{(\text{PH})}$ value of 10 or less Hz [7, 11]. Moreover, the $^31\text{P}\{^1\text{H}\}$ -NMR spectra of complexes (1)–(4) show a sharp singlet at 16 ppm, shifted slightly up field relative to the free ylide and again in agreement with O-coordination [6, 12–15].

The $^31\text{PNMR}$ resonance of complex (5) occurs at lower field with respect to the free ylide (Table 2). The expected

Scheme 2 (1) R = MeO, L = PPh_3 ; (2) R = F, L = PPh_3 ; (3) R = MeO, L = pyridine; (4) R = MeO, L = 3-methyl pyridine

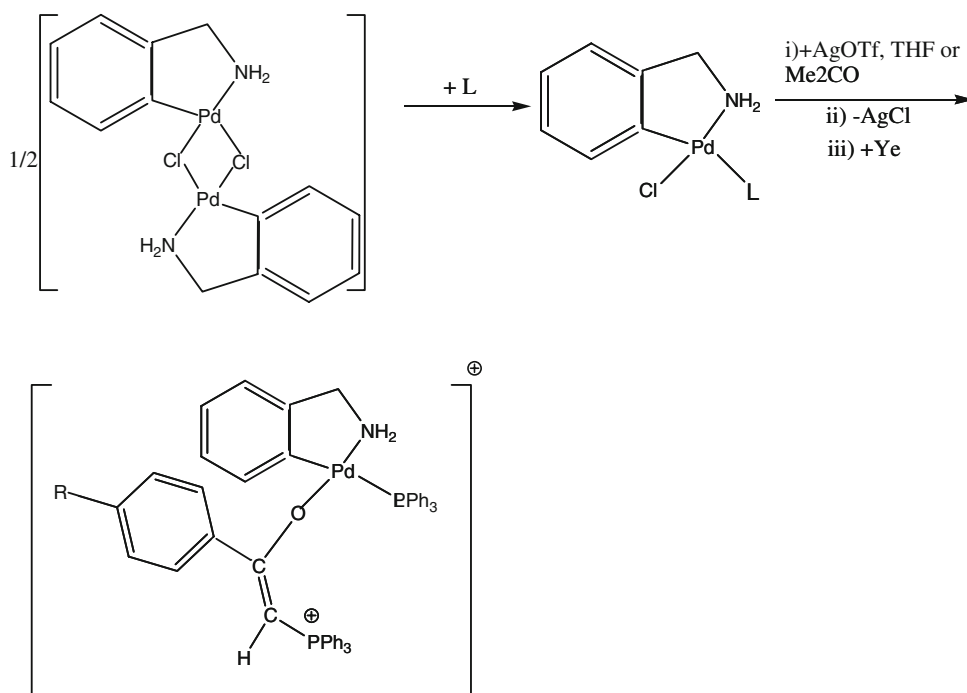


Table 1 $\nu(\text{CO})$ frequencies of selected phosphoranes and their metal complexes

Compound	$\nu(\text{CO})$	$\Delta(\text{CO})$	$\nu(\text{P}-\text{C})$	Reference
$\text{Ph}_3\text{PCHCOCH}_3$ (APPY)	1530	–		[19]
$\text{Ph}_3\text{PCHCOPh}$ (BPPY)	1520	–	878	[19]
$\text{Ph}_3\text{PCHCOC}_6\text{H}_4\text{-OMe}$ (=MOBPPY)	1504	–	855	This work
$\text{Ph}_3\text{PCHCOC}_6\text{H}_4\text{-F}$ (=FBPPY)	1516		883	This work
O-coordination				
$[(\text{Sn}(\text{CH}_3)_3 \cdot \text{APPY})\text{Cl}]$	1480	–40	–	[12]
$[\text{Pd}\{\text{C}_6\text{F}_5\}(\text{PPh}_3)_2$ $(\text{APPY})\text{ClO}_4]$	1513	–17	–	[7]
Complex (1)	1479	–25	821	This work
Complex (2)	1481	–37	817	This work
Complex (3)	1475	–29	808	This work
Complex (4)	1480	–24	824	This work
C-coordination				
Complex (5)	1612	+96	880	This work
$\text{BPPY} \cdot \text{HgCl}_2$	1635	+115	–	[20]
$\text{BPPY} \cdot \text{HgBr}_2$	1630	+110	–	[20]

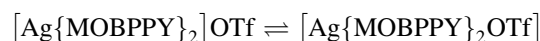
Abbreviations: MOBPPY, 4-methoxybenzoylmethylenetriphenylphosphorane; FBPPY, 4-fluorobenzoylmethylenetriphenylphosphorane; BPPY, benzoylmethylenetriphenylphosphorane; APPY, acethylmethylcenetriphenylphosphorane

downfield shifts of ^{31}P and ^1H signals for the PCH group upon complexation were observed in their corresponding spectra. The appearance of single signals for the PCH group in both the ^{31}P and ^1H NMR at ambient temperature indicates the presence of only one molecule for all the complexes. It must be noted that O-coordination of the ylide sometimes leads to the formation of *cis* and *trans* isomers, giving rise to two different signals in the ^{31}P and ^1H NMR [6, 18]. ^1H and $^{31}\text{P}\{-^1\text{H}\}$ NMR data are presented in Table 2. Although two diastereoisomers (RR/SS and RS) are possible for complex (5) (because the methine carbons are chiral), NMR spectroscopy does not distinguish them at room temperature. The methine resonances are intermediate between, and $^2J_{(\text{PH})}$ values smaller than, those in the free ylides and phosphonium salts; this was observed for other C-coordinated carbonyl-stabilized phosphorus ylide complexes: it is attributed the hybridization change in the ylidic carbon ($\text{sp}^2\text{-sp}^3$) in the C-coordination mode [7, 15, 17]. Values of $^2J_{(\text{PH})}$ much larger (ca. 20 Hz) have been observed in complex (1) where coordination is through the oxygen atom [12]. Neither H–Ag nor P–Ag coupling was observed at room temperature in the spectra of complex (5); the same was the case for $[\text{Ag}(\text{C}_6\text{F}_5)\text{CH}(\text{PPh}_3)\text{CO}_2\text{Me}]$ [19]. It is possible that a fast equilibrium between the complexes and free ylides is responsible for the failure to observe either the NMR

Table 2 ^1H and ^{31}P NMR data of MOBPPY and its complexes with Ag(I) and Pd(II)

Compound	^1H chemical shifts (CH) (δ ppm)	$^2J_{(\text{PH})}$ (Hz)	^{31}P chemical shifts (δ ppm)
MOBPPY	4.37 (d)		16.8
Complex (1)	4.4 (br)	–	14.06, 40.93
Complex (2)	4.4 (br)	–	13.68, 41.28
Complex (3)	4.5 (d)	25	16.00
Complex (4)	4.35 (s br)	–	16.16
Complex (5)	5.22 (s br)	–	24.75

couplings or presence of two diastereoisomers. The molar conductivities of (1)–(4) are within the range for 1:1 electrolytes [21], while the low value found for complex (5) can be explained by assuming that the anion interacts with the cation complex in solution [11]:



Conclusion

Complexes (1)–(4) represent new examples of ylides O-bound to a soft metal center. This coordination mode is rather unusual for the classical soft metals. It seems likely that the cationic character of the palladium complexes renders the metal center less soft and more receptive to possible coordination by a hard ligand. On the other hand, the O-coordination of the ylide results in lower steric requirements than the C-coordination mode. The compromise between electronic and steric factors would decide the final coordination mode of the ylide. Examples of C-coordination of ylide in cationic Pd(II) complexes are known [10], showing that the cationic character of the complex is not the only parameter to be considered. In complex (5), the ylide ligand binds to the silver atom through the methine carbon. This coordination mode is also rather usual for the classical soft metals.

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