Synthesis and Characterization of {Pd(dmba)-(py)[OC(CH₃)=C(H)PPh₃]}(ClO₄)·CH₂Cl₂. Unusual O-Coordination of the (Acetylmethylene)triphenylphosphorane Ligand to a Soft Metal Center

Larry R. Falvello, Susana Fernández, Rafael Navarro,* and Esteban P. Urriolabeitia

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, CSIC 50009 Zaragoza, Spain

Introduction

The organometallic chemistry of phosphorous ylides $R_3P=C(R')(R'')$ (R, R′, R″ = alkyl or aryl groups) has undergone a great growth in the last few years, mainly due to their interesting applications as reactants in organometallic and metal-mediated organic synthesis.[1] On the whole, the α-keto-stabilized phosphorous ylides $R_3P=C(R')COR''$ show interesting properties such as their high stability (which allow them to be easily handled in air) and their ambidentate character as ligands (*C*-vs *O*-coordination). This ambidentate character can be rationalized in terms of the resonance forms **A**−**C**, together with the isomeric form **D** (Chart 1). Form **B** would account for the *C*-coordination (which is presented in Chart 2 as **G**) while isomers **C** and **D** would explain *O*-coordination (which are presented in Chart 2 as cisoid, form **F**, and transoid, form **E**, respectively).

In the compounds reported to date, the chemical behavior of the α-keto phosphorous ylides has been clearly dominated by the *C*-coordinated form,[1,2] and very few examples of *O*-coordinated ylides are known.[3] Some of these examples contain the ylide *O*-coordinated to a hard, very oxophilic metal center, as Sn(IV)[3a,b] or group 4 metals in high oxidation number.[3e] Only W(0) complexes of the type $W(CO)_5L$ (L = ylide)[3c] and Pd(II) complexes of stoichiometry $[Pd(C_6F_5)L_2(APPY)](ClO_4)$[3d] [APPY = $Ph_3PC(H)COMe$; L = PPh_3, P^nBu_3; L_2 = bipy] contain stable ylides *O*-linked to a soft metal center. Other attempts to obtain
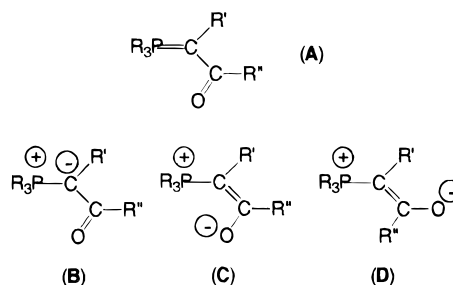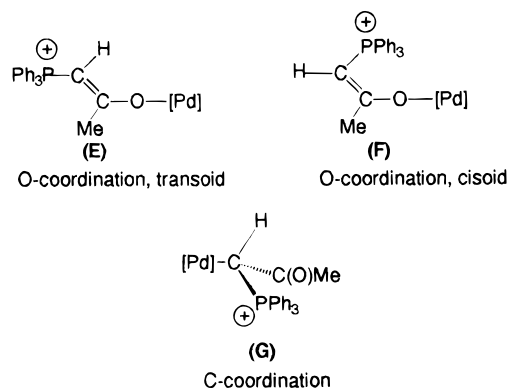
Chart 1

Chart 2

this kind of coordination to "classical" soft metals such as Pd(II), Pt(II), or Hg(II)[2b,4] invariably gave *C*-coordination.

This paper presents our initial results on the reactivity of solvated species of stoichiometry $[Pd(dmba)(L)(THF)](ClO_4)$ [dmba = 2-((dimethylamino)methyl)phenyl-C^1,*N*, L = neutral ligand, and THF = tetrahydrofuran] toward α-keto-stabilized phosphorous ylides, which gives cationic Pd(II) complexes containing the *O*-bound ylide. We report here the synthesis, spectroscopic characterization, and X-ray crystal structure determination of {Pd(dmba)(py)[OC(CH₃)=C(H)PPh₃]}(ClO₄), which represents the first structurally characterized ylide coordinated through oxygen to a soft metal center.

Results and Discussion

When a freshly prepared solution of [Pd(dmba)(py)(THF)]-(ClO₄) is allowed to react with (acetylmethylene)triphenylphosphorane (APPY) (1:1 molar ratio) in THF at 0 °C, a white solid of stoichiometry [Pd(dmba)(py)(APPY)](ClO₄) (**1**) precipitates in good yield after 20 min of stirring. Spectroscopic techniques such as IR and NMR spectroscopy enable one to distinguish between *O*(carbonyl) and *C*(methine)-coordination. The IR spectrum of (**1**) shows an intense absorption at 1506 cm⁻¹, corresponding to the stretching $\nu(C=O)$. This absorption has been shifted to lower energies with respect to the free ylide $[\Delta\nu = \nu(CO)_{comp} - \nu(CO)_{free\ ylide} = 1506 - 1540 = -34\ cm^{-1}]$. Bonding through the carbonyl oxygen implies a major contribution of the isomeric forms **C** and **D** and a decrease in the carbonyl stretching frequency,[3] as we observe in **1**. This suggests that the ylide is *O*-bound. NMR spectroscopy provides additional information. The ¹H NMR spectrum shows a doublet resonance attributed to the methine proton C*H* at 4.17 ppm. with a coupling constant $^2J_{P-H} = 24$ Hz; this value is close to those observed in other *O*-bound complexes[3c−e] (this coupling

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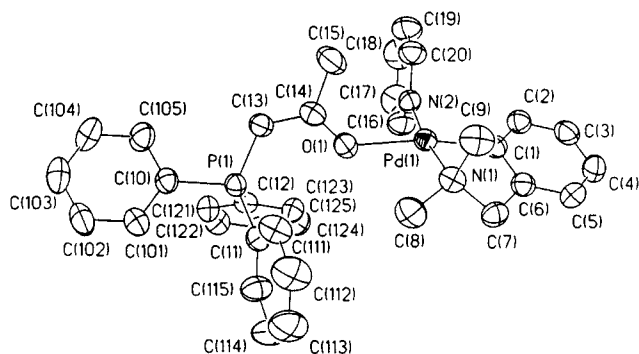
Figure 1. Thermal ellipsoid plot of the {Pd(dmba)(py)[OC(CH₃)=C(H)-PPh₃]}⁺ cation. Atoms are drawn at the 50% probability level.

Table 1. Crystal Data for **1**·CH₂Cl₂

formula	C₃₆H₃₈Cl₃N₂O₅PPd	d_{calc}, g/cm³	1.488
cryst syst	triclinic	cryst size, mm	0.46 × 0.29 ×
space group	$P\bar{1}$		0.29
fw	822.40	μ, mm⁻¹	0.811
a, Å	11.1353 (5)	no. of unique rflcns	6426
b, Å	12.7720 (8)	no. of rflcns with	5606
c, Å	13.5235 (8)	$I > 2\sigma(I)$	
α, deg	75.103 (5)	no of variables	482
β, deg	81.255 (4)	R1ᵃ	0.0370
γ, deg	85.308 (3)	wR2ᵃ	0.0890
Z	2	GOF	1.068
F(000)	840	max shift/σ	−0.026
V, Å³	1835.2(2)	res electron density	0.35 e/Å³

ᵃ R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. GOF = $[\sum w (F_o^2 - F_c^2)^2/(n_{observns} - n_{params})]^{1/2}$.

constant has lower values in *C*-linked ylides). Moreover, the ³¹P{¹H} NMR spectrum shows a sharp singlet resonance at 13.40 ppm, shifted slightly upfield relative to the free ylide and again in agreement with *O*-coordination,[3d,e] because *C*-coordination would result in a downfield shift of about 10 ppm of the ylide resonance.[2j,l] Finally, in the ¹³C{¹H} NMR spectrum the resonance attributed to the methine carbon appears as a doublet at 60.1 ppm (shifted downfield relative to the free ylide) with a coupling constant $^1J_{P-C}$ = 106 Hz, very similar to that observed in the free ylide. This result is also in agreement with *O*-coordination.[3e] In all of the spectra, only one of the two possible isomers [transoid (**E**)/cisoid (**F**) (see Chart 2)] is detected. We have not observed isomerization into the *C*-bound form, or decomposition, even after 1 week in CD₂Cl₂ solution, proof of the high stability of the product. The elucidation of the conformation of the ylide has been accomplished by means of an ¹H−¹H 2D-NOESY measurement. Therein, the methine C*H* resonance shows a strong nOe interaction with the resonance of the methyl group of the ylide ligand, indicating the proximity of the interacting nuclei. In addition, the methyl (ylide) resonance shows a very weak nOe interaction with the Ph groups. A cisoid conformation for the *O*-bonded ylide accounts for these results.

The molecular structure of **1**·CH₂Cl₂ (crystals obtained by slow diffusion of *n*-hexane into a CH₂Cl₂ solution of **1** at room temperature) provides further characterization. A drawing of the cationic complex is shown in Figure 1 and selected bond distances and angles are collected in Table 2. The palladium atom is located in a slightly distorted square-planar environment, surrounded by the C and N atoms of the cyclometalated dmba ligand, the N atom of the pyridine, and the carbonyl oxygen of the ylide. As can be seen, the ylide is bonded to the Pd center through the carbonyl oxygen and adopts the cisoid conformation, in agreement with the results obtained from the solution studies. The Pd−C(1) (dmba) and Pd−N(1) (dmba) distances are similar

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**·CH₂Cl₂

Bond Distances					
Pd(1)−C(1)	1.974(3)	Pd(1)−N(2)	2.046(3)	Pd(1)−N(1)	2.074(3)
Pd(1)−O(1)	2.154(2)	P(1)−C(13)	1.732(3)	C(13)−C(14)	1.366(4)
C(14)−O(1)	1.275(4)	C(14)−C(15)	1.500(5)		

Bond Angles			
C(1)−Pd(1)−N(2)	91.37(12)	C(1)−Pd(1)−N(1)	82.21(12)
N(2)−Pd(1)−O(1)	91.83(10)	N(1)−Pd(1)−O(1)	94.96(10)
C(14)−C(13)−P(1)	123.9(3)	O(1)−C(14)−C(13)	123.1(3)
O(1)−C(14)−C(15)	118.1(3)	C(13)−C(14)−C(15)	118.8(3)
C(14)−O(1)−Pd(1)	133.6(2)		

to those found in other Pd(dmba) complexes[5] and the Pd−N(2) distance falls also in the usual range found for this bond.[6] The Pd-O(1) distance is 2.154(2) Å. The P(1)−C(13) (methine) distance is 1.732(3) Å, shorter than the average P−C(Ph) single bond distance (1.807 Å), thus indicating that there remains some multiple bond character, albeit slight. As a comparison, the P−C bond distance found in the ylide Ph₃P=CH₂ is 1.66 Å, which corresponds to a bond order of 1.33,[7] and those found in the related complexes [SnMe₃Cl(APPY-*O*)][3a] and *trans*-[TiCl₄-(APPY-*O*)(THF)]·THF[3e] are 1.75 and 1.774(7) Å, respectively. The C(13)-C(14) bond distance is 1.366 (4) Å, which indicates double-bond character, in keeping with the major contribution of the resonance form **C** (Chart 1) in this bonding mode. This distance is similar, within experimental error, to those found in [SnMe₃Cl(APPY-*O*)][3a] (1.36 Å) and *trans*-[TiCl₄(APPY-*O*)-(THF)]·THF[3e] [1.333(9) Å]. The C(14)−O(1) bond distance is 1.275(4) Å, similar to that reported for *trans*-[SnMe₃Cl-(APPY-*O*)][3a] (1.27 Å) and shorter than that observed in *trans*-[TiCl₄(APPY-*O*)(THF)]·THF[3e] [1.332(8) Å], although it is still longer than the C−O bond distances found in the *C*-bound ylides.[2]

In conclusion, complex **1** represents the first example of an ylide *O*-bound to a soft metal center whose structure has been confirmed by a single-crystal X-ray diffraction study. This coordination mode is rather unusual for the classical soft metals, in the sense that a classical "hard" atom is bonded to a "soft" metal. In our case, this is the experimental evidence, and the reasons for which an ylide selectively adopts one coordination mode in these metals and the role of the electronic and steric factors remain unclear. We think that the cationic character of the palladium complex 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 these factors would decide the final coordination mode of the ylide. For instance, examples of *C*-coordination of the ylide in cationic Pd(II) complexes are known,[2f,j] showing that the cationic character of the complex is not the only parameter to be considered. In our case, we think that both the cationic character and the steric requirements of the complex [Pd(dmba)(py)(THF)]⁺ favor the *O*-coordination mode.

Also, it is interesting to note that different precursors such as [Pd(OClO₃)(C₆F₅)L₂],[3d] which contains the electron-withdrawing C₆F₅ group and the very weakly coordinated OClO₃⁻ ligand, and [Pd(dmba)(py)(THF)](ClO₄), which contains essentially σ-donor ligands, react with the ylides to give the same type of *O*-bonded derivatives. In order to obtain a better understanding of the chemical behavior of the ylides, further studies on the reactivity of the complexes [Pd(dmba)(L)(THF)]-

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(ClO$_4$) (L = neutral ligands) with different α-keto-stabilized ylides are now in progress.

Experimental Section

Safety Note. *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and they should be handled with great caution. See ref 12.

Materials. Solvents were dried and distilled before use by standard methods. Elemental analyses were carried out on a Perkin -Elmer 240-B microanalyzer. IR spectra (4000−200 cm^{-1}) were recorded from Nujol mulls between polyethylene sheets on a Perkin-Elmer 883 spectrophotometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300.13 and 75.47 MHz, respectively, from CD$_2$Cl$_2$ solutions at room temperature on a Bruker ARX-300 spectrometer using the solvent signal as internal standard. ^{31}P{^{1}H} NMR spectra were recorded at 121.49 MHz from CD$_2$Cl$_2$ solutions at room temperature on a Bruker ARX-300 spectrometer and referenced to H$_3$PO$_4$ (85%). The two-dimensional ^{1}H-^{1}H NOESY experiment was performed at a measuring frequency of 300.13 MHz. The data were acquired into a 512 × 1024 matrix, and then transformed into 1024 × 1024 points using a sine window in each dimension (mixing time 400 ms). Mass spectrum (positive ion FAB) was recorded on a VG-Autospect spectrometer. The starting compounds [PdCl(dmba)(py)][8] and Ph$_3$P=C(H)C(O)Me[9] were obtained as previously reported.

{Pd(dmba)(py)[OC(CH$_3$)=C(H)PPh$_3$]}(ClO$_4$) (1). To a solution of PdCl(dmba)(py) (0.200 g, 0.563 mmol) in THF (20 mL) was added AgClO$_4$ (0.117 g, 0.563 mmol). The resulting suspension was stirred for 20 min at room temperature and filtered. To the freshly obtained solution, cooled at 0 °C, was added Ph$_3$P=C(H)COMe (0.179 g, 0.563 mmol). After 20 min of stirring at 0 °C, the complex (**1**) precipitated as a white solid, which was filtered and air-dried. Yield: 71%. **1**·CH$_2$-Cl$_2$ recrystallized from CH$_2$Cl$_2$/*n*-hexane was used for elemental analysis and NMR measurements. Anal. Calcd for C$_{36}$H$_{38}$Cl$_3$N$_2$O$_5$PPd: C, 52.57; H, 4.67; N, 3.40. Found: C, 52.26; H, 4.59; N, 3.38. MS (+FAB) [*m/z*, (%)]: 637 (11%) [M$^+$], 558 (27%) [(M−py)$^+$]. IR (ν_{CO}): 1506 cm^{-1}. NMR: ^{1}H δ, 8.28 (d, 2H, py, $^3J_{H-H}$ = 4 Hz), 7.98 (t, 1H, py, $^3J_{H-H}$ = 7 Hz), 7.70−7.50 (m, 15H, Ph), 7.40 (t, broad, 2H, py), 6.96 (m, 2H, C$_6$H$_4$), 6.72 (false t, 1H, C$_6$H$_4$, $^3J_{H-H}$ = 6 Hz), 5.88 (d, 1H, C$_6$H$_4$, $^3J_{H-H}$ = 8 Hz), 4.17 (d, 1H, =CH, $^2J_{P-H}$ = 24 Hz), 3.87 (s, 2H, CH$_2$N), 2.29 (s, 6H, NMe$_2$), 2.11 (s, 3H, =CMe); ^{31}P{^{1}H} δ, 13.40 (s, −P$^+$Ph$_3$); ^{13}C {^{1}H} δ, 190.7 (CO), 153.1, 139.4, 126.3 (NC$_5$H$_5$), 150.5, 148.2, 144.8, 133.1, 125.8, 122.2 (C$_6$H$_4$), 133.6 ($^3J_{P-C}$ = 7 Hz), 133.5, 129.7 ($^2J_{P-C}$ = 15 Hz), 124.9 ($^1J_{P-C}$ = 38 Hz) (PPh$_3$), 73.2 (CH$_2$N), 60.1 (=CH, $^1J_{P-C}$ = 106 Hz), 51.5 (NMe$_2$), 29.3 (=C*Me*, $^3J_{P-C}$ = 14 Hz).

X-ray Data Collection. A colorless, block-shaped crystal was mounted at the end of a glass fiber and covered with epoxy. Geometric and intensity data were taken using normal procedures on an automated Enraf Nonius CAD-4 four-circle diffractometer (graphite-monochro-mated Mo Kα; $2\theta_{max}$ = 50°). After initial indexing of the cell, axial photos were taken for the axes *a*, *b*, *c*, and [111] in order to check the lattice dimensions. A hemisphere of intensity data was gathered, using a variable scan-speed technique in which the weakest data were measured at the slowest scan speed. That is to say, no measurement was skipped or measured rapidly because of weak diffraction. The scan parameters for intensity data collection were chosen on the basis of two-dimensional ($\omega-\theta$) plots of 25 reflections. Azimuthal scans of 11 scattering vectors were used as the basis of an absorption correction. A correction was also applied to account for a 3% variation in three monitor reflections that were remeasured every 3 h during data collection.

Structure Solution and Refinement. After data reduction, all non-hydrogen atoms of one asymmetric unit, except for the atoms of a disordered interstitial CH$_2$Cl$_2$ moiety, were located by an automated procedure that incorporates Patterson analysis, difference direct methods, and Fourier peaklist optimization.[10] The structure was refined to F_o^2, and all positive data were used in the refinement.[11] The hydrogen atoms of the cation were placed in idealized positions and treated as riding atoms, except for those of the methyl groups, which were first located in a local slant-Fourier calculation and then refined as riding atoms with the torsion angles about the C−C(methyl) or N−C(methyl) bonds treated as variables. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The perchlorate anion was found to have a disordered minor component, and the relative occupancies of the two congeners refined to values of approximately 0.9 and 0.1. Two oxygen atoms were common to the two components. The displacement parameters of the two congeners were constrained to equality. The geometrical parameters of the minor component were restrained to be similar to those of the major component. An interstitial molecule of CH$_2$Cl$_2$ was also found to be disordered, and was modelled as three equally populated congeners occupying the same interstice, and with a common carbon atom. No constraints or restraints were needed for the solvent. The refinement converged with the residuals shown in Table 1. The largest peak on a final difference Fourier map had a density of about one-third electron/Å^3.

Supporting Information Available: Tables of crystallographic data, atomic coordinates, bond lengths and angles, anisotropic thermal parameters and hydrogen atom coordinates (6 pages). Ordering information is given on any current masthead page.

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