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Nucleophilic Attack of Carbonyl-Stabilized Phosphorus Ylides on 1,5-Cyclooctadiene Complexes of Palladium and Platinum

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Carbonyl-stabilized phosphorus ylides $R_3P{=}CHC(O)R'$ (R = Ph, Tol-*p*; R′ = OEt, OMe, NMe_2) react with the 1,5-cyclooctadiene complexes $[MCl_2(cod)]$ (M = Pt, Pd; cod = C_8H_{12} = 1,5-cyclooctadiene) to give the monomeric cyclooctenyl complexes $[MCl_2\{C_8H_{12}\{CH(PR_3)C(O)R'\}\}]$. The ylides attack in an *exo* fashion to give complexes which can be regarded as metalated phosphonium salts. Reactions involving the replacement of one or both chloro ligands with a neutral ligand are discussed. The crystal structures of complexes $[PtCl_2\{C_8H_{12}\{CH(PPh_3)CO_2Me\}\}]$ and $[Pt\{C_8H_{12}\{CH(PPh_3)CO_2Me\}\}(py)_2](CF_3SO_3)_2$ are reported.

Introduction

Nucleophilic attack at olefinic bonds coordinated to palladium(II) or platinum(II) has been well studied[1,2] and found to be the key step in many catalytic reactions. A wide range of nucleophiles including HO^-,[3,4] RO^-,[3,5] RCO_2^-,[3,4,6] N_3^-,[7,8] H^-,[9] Cl^-,[6,10] NR_nH_{3-n},[6,11] CN^-,[8] NCO^-,[7,8,12] NO_2^-,[5,7,8,13] aryl,[3,5,14−16] acetylacetonate,[5,17] diethylmalonate, ethyl acetoacetate,[17] and *N*,*N*-dimethylaminonaphthalene[18] (Proton Sponge) have been employed, and enhanced electrophilicity of the olefinic moiety in cationic complexes has been observed.[8] Although phosphorus ylides have never been used in these reactions, a couple of examples were reported in which an (ethylene)iron(II) complex was attacked by an ylide to give a metalated phosphonium complex.[19,20] In most cases the attack is produced in an *exo* fashion to give complexes in which the nucleophile is *anti* with respect to the metal. Only a few examples of *endo* attack have been reported,[5,9,13−16] in which attack of the nucleophile to the metal followed by migratory insertion of the double bond has been invoked. In the vast majority of cases (in all for norbornadiene or 1,5-cyclooctadiene complexes), the nucleophilic attack produces a dinuclear chloro-bridged enyl complex.

Our interest in this type of reaction stems from previous research[21] in which we found that the reactions of $[PtCl_2(NCPh)_2]$ with the carbonyl-stabilized phosphorus ylides $Ph_3P{=}CHCO_2R$ (R = Me, Et) did not give the expected $[PtCl_2\{CH(PPh_3)CO_2R\}_2]$ complexes. Instead, we obtained complexes $[PtCl_2(L)(NCPh)]$ with one iminophosphorane ligand L = $N({=}PPh_3)C(Ph){=}CHCO_2R$ resulting from the nucleophilic attack of the benzonitrile ligand by the ylide. This led to further research,[22] yielding a range of platinum(II) complexes containing N-bonded iminophosphorane $[N({=}PPh_3)C(C_6F_5){=}CHCO_2R]$ and/or N-bonded-β-iminophosphorus ylide $[NH{=}C(C_6F_5)C({=}PPh_3)CO_2R]$ ligands.

In this paper we report the reactions of carbonyl-stabilized phosphorus ylides $R_3P{=}CHC(O)R'$ (R = Ph, C_6H_4Me-4; R′ = OEt, OMe, NMe_2) with $[MCl_2(COD)]$ (M = Pt, Pd; COD = C_8H_{12} = 1,5-cyclooctadiene). These lead not to the expected $[MCl_2\{CH(PR_3)C(O)R\}_2]$ but to

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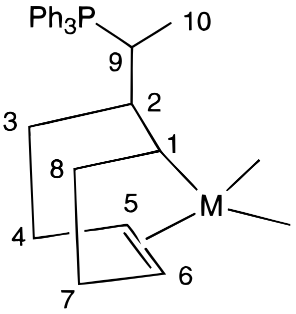
Chart 1. Numbering Scheme for NMR Assignments



monomeric complexes (resulting from the nucleophilic attack of the COD ligand by the ylide) which can be regarded as metalated phosphonium salts. The complex [PtCl$_2${C$_8$H$_{12}${CH(PPh$_3$)CO$_2$Me}}] has been characterized by X-ray crystallography, and its structure is discussed. We also report some reactions of these complexes involving the replacement of one or both chloro ligands with pyridine (py) and the resultant mono- and dicationic derivatives. The complex [Pt{C$_8$H$_{12}${CH(PPh$_3$)CO$_2$Me}}(py)$_2$](CF$_3$SO$_3$)$_2$ has been characterized by X-ray crystallography.

Experimental Section

The IR spectra, elemental analyses, conductance measurements in acetone, and melting point determinations were carried out as described earlier.[23] Unless otherwise stated, the reactions were carried out at room temperature without special precautions against moisture. Technical grade solvents were purified by standard procedures. The ^{1}H, and ^{31}P{^{1}H} NMR spectra were recorded with Varian Unity-300 or Bruker AC-200 spectrometers, and chemical shifts are referred to TMS (^{1}H) or H$_3$PO$_4$ [^{31}P{^{1}H}]. The assignments are according to the numbering in Chart 1. C$_6$H$_4$Me-4 = To.

Syntheses of [PtCl$_2${C$_8$H$_{12}${CH(PPh$_3$)C(O)R}}] [R = OMe(1a), OEt (1b), NMe$_2$ (1c)]. To a rapidly stirring solution of [PtCl$_2$(COD)] (ca. 0.3−0.6 mmol) in acetone (20 mL) was added the equimolar amount of the ylide Ph$_3$P═CHC(O)R. The reaction mixture was allowed to stir for 24 (**1a, c**) or 14 (**1b**) h, during which time the solution became turbid. It was concentrated (to ca. 2 mL) under reduced pressure, and diethyl ether (25 mL) was added to yield complexes **1a**−**c** as white solids, which were washed with diethyl ether (2 × 5 mL) and suction dried. Crystals of **1a**·3CDCl$_3$ suitable for an X-ray diffraction study were grown by slow evaporation of a solution of **1a** in CDCl$_3$.

1a: Yield, 76%; mp, 173 °C. Anal. Calcd for C$_{29}$H$_{31}$Cl$_2$O$_2$PPt: C, 49.16; H, 4.41. Found: C, 49.00; H, 4.24. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.06−2.17 (m, 8 H, H3, H4, H7, H8), 2.84 (m, 1 H, H2), 3.19 ("d", 1 H, H1, $^3J_{HH}$ = 6 Hz), 3.54 (s, 3 H, Me), 4.45 (d, 1 H, H9, $^2J_{HP}$ = 12.00 Hz), 4.60 (m, 1 H, H5), 4.76 (m, 1 H, H6), 7.59−7.84 (m, 15 H, Ph). ^{31}P{^{1}H} NMR (300 MHz, CDCl$_3$): δ 24.23 (s). FAB MS: *m/z* (%, abundance): 672 (M$^+$ − Cl, 16), 441 (M$^+$ − Pt − 2Cl, 9). IR (cm^{-1}) ν(CO): 1724.

1b: Yield, 79%; mp, 210 °C. Anal. Calcd for C$_{30}$H$_{33}$Cl$_2$O$_2$PPt: C, 49.87; H, 4.60. Found: C, 50.32; H, 4.38. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.04−2.13(m, 8 H, H3, H4, H7, H8), 1.14 ("t", 3 H, CH$_2$*Me*, $^3J_{HH}$ = 7.13 Hz], 2.86 (m, 1H, H2), 3.21 [(d, 1 H, H1, $^3J_{HH}$ = 4.2 Hz), 4.02 (m, 2 H, C*H*$_2$Me), 4.43 (d, 1 H, H9, $^2J_{HP}$ = 11.45 Hz), 4.63 (m, 1 H, H5), 4.77 (m, 1 H, H6), 7.71−7.86 (m, 15 H, Ph). ^{31}P{^{1}H} NMR (300 MHz, CDCl$_3$): δ 24.26 (s). FAB MS: *m/z* (% abundance): 686 (M$^+$ − Cl, 64), 455 (M$^+$ − Pt − 2Cl, 39), 349 [CH(PPh$_3$)CO$_2$Et, 79], 303 [Pt(COD), 100]. IR (cm^{-1}) ν(CO): 1718.

1c: Yield, 72%; mp, 131 °C. Anal. Calcd for C$_{30}$H$_{34}$Cl$_2$NOPPt: C, 49.94; H, 4.75; N, 1.94. Found: C, 49.38; H, 4.77; N, 2.08. ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.20−2.16 (m, 8 H, H3, H4, H7, H8), 2.72 (s, 3 H, Me), 2.90 (m, 1H, H2), 3.30 (m 3H, Me), 3.32 (m, 1 H, H1), 4.55 (m, 1 H, H5), 4.75 (m, 1 H, H6), 4.91 (d, 1 H, H9, $^2J_{HP}$ = 12.4 Hz), 7.61−7.91 (m, 15 H, Ph). ^{31}P{^{1}H} NMR (300 MHz, CDCl$_3$): δ 24.90 (s). FAB MS: *m/z* (% abundance): 686 (M$^+$ − Cl, 60), 454 (M$^+$ − Pt − 2Cl, 30). IR (cm^{-1}) ν(CO): 1634.

Syntheses of [PdCl$_2${C$_8$H$_{12}${CH(PR$_3$)C(O)R′}}] [R = Ph, R′ = OMe(2a), OEt (2b), R = To, R′ = OMe(2a′), OEt (2b′)]. To a rapidly stirring solution of [PdCl$_2$(COD)] (ca. 0.4−0.8 mmol) in acetone (20 mL) was added the equimolar amount of the ylide R$_3$P═CHC(O)R′. The reaction mixture was allowed to stir for 24 (**2a, 2b, 2a′**) or 4 (**2b′**) h, during which time the color of the solution lightened and a precipitate formed. The suspension was concentrated (to ca. 2 mL) under reduced pressure, and diethyl ether (25 mL) was added to complete precipitation of complexes **2a, 2b, 2a′,** and **2b′** as pale yellow solids, which were washed with diethyl ether (2 × 5 mL) and suction dried. **2a** was chromatographed on silica gel using acetonitrile as the eluent.

2a: Yield, 74%; mp, 239 °C. Anal. Calcd for C$_{29}$H$_{31}$Cl$_2$O$_2$PPd: C, 56.19; H, 5.04. Found: C, 56.08; H, 5.18. ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.02−2.11 (m, 8 H, H3, H4, H7, H8), 2.87 (m, 1 H, H2), 3.54 (s, 3 H, Me), 3.90 (d, 1 H, H1, $^3J_{HH}$ = 5.8 Hz), 4.59 (d, 1 H, H9, $^2J_{HP}$ = 11.6 Hz), 5.51 (m, 1 H, H5), 6.01 (m, 1 H, H6), 7.70−7.81 (m, 15 H, Ph). ^{31}P{^{1}H} NMR (300 MHz, CDCl$_3$): δ 23.71 (s). FAB MS: *m/z* (% abundance): 585 (M$^+$ − Cl, 20), 441 (M$^+$ − Pd − 2Cl, 100). IR (cm^{-1}) ν(CO): 1720.

2b: Yield, 81%; mp, 210 °C. Anal. Calcd for C$_{30}$H$_{33}$Cl$_2$O$_2$PPd: C, 56.85; H, 5.25. Found: C, 56.69; H, 5.38. NMR (300 MHz, CDCl$_3$): δ 1.04−2.32 (m, 8 H, H3, H4, H7, H8), 1.10 (m, 3 H, CH$_2$*Me*), 2.84 (m, 1 H, H2), 3.80−4.10 (m, 3 H, H1, C*H*$_2$Me), 4.52 (d, 1 H, H9, $^2J_{HP}$ = 11.7 Hz), 5.51 (m, 1 H, H5), 6.00 (m, 1 H, H6), 7.60−7.95 (m, 15 H, Ph). ^{31}P{^{1}H} NMR (300 MHz, CDCl$_3$): 23.71 (s). FAB MS: *m/z* (% abundance): 599 (M$^+$ − Cl, 13), 455 (M$^+$ − Pd − 2Cl, 50), 154 (Ph$_2$, 100). IR (cm^{-1}) ν(CO): 1720.

2a′· 0.5CH$_2$Cl$_2$: Yield, 70%; mp, 176 °C. Anal. Calcd for C$_{32.5}$H$_{38}$Cl$_3$O$_2$PPd: C, 55.42; H, 5.44. Found: C, 55.70; H, 5.23. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.07−2.33 (m, 8 H, H3, H4, H7, H8), 2.41 (s, 9 H, C$_6$H$_4$*Me*-4), 2.76 (m, 1 H, H2), 3.51 [s, 3 H, C(O)*Me*], 3.86 (m, 1 H, H1), 4.40 (d, 1 H, H9, $^2J_{HP}$ = 11.7 Hz), 5.22 (s, 1 H, C*H*$_2$Cl$_2$), 5.51 (m, 1 H, H5), 6.01 (m, 1 H, H6), 7.42−7.70 (m, 12 H, Ph). ^{31}P{^{1}H} NMR (300 MHz, CDCl$_3$): δ 22.89 (s). FAB MS: *m/z* (% abundance): 626 (M$^+$ − Cl, 10), 483 (M$^+$ − Pd − 2Cl, 69). IR (cm^{-1}) ν(CO): 1714.

2b′: Yield, 68%; mp 122 °C. Anal. Calcd for C$_{33}$H$_{39}$Cl$_2$O$_2$PPd: C, 58.74; H, 5.83. Found: C, 58.57; H, 6.01. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.04−2.23 (m, 8 H, H3, H4, H7, H8), 1.13 ("t", 3 H, CH$_2$*Me*), 2.47 (s, 9 H, C$_6$H$_4$*Me*-4), 2.80 (m, 1 H, H2), 3.95 (d, 1 H, H1, $^3J_{HH}$ = 6.4 Hz), 4.02 (m, 2 H, C*H*$_2$Me), 4.43 (d, 1 H, H9, $^2J_{HP}$ = 11.8 Hz), 5.58 (m, 1 H, H5), 6.08 [m, 1 H, H(6)], 7.45−7.73 (m, 12 H, Ph). ^{31}P{^{1}H} NMR (300 MHz, CDCl$_3$): δ 22.89 (s). FAB MS: *m/z* (% abundance): 640 (M$^+$ − Cl, 12), 497 (M$^+$ − Pd − 2Cl, 54), 391 [CH(PTo$_3$)CO$_2$Et, 100]. IR (cm^{-1}) ν(CO): 1706.

Synthesis of [PtCl{C$_8$H$_{12}${CH(PPh$_3$)CO$_2$Et}(py)]ClO$_4$ (3). Silver perchlorate (43 mg, 0.207 mmol) was added to a stirring solution of **1b** (150 mg, 0.207 mmol) in dichloromethane (20 mL), and the resulting suspension was filtered after 30 min of stirring. Upon addition of pyridine (py) (18 mg, 0.227 mmol) to the solution, its color changed from pale yellow to colorless. After 2 h, the solvent was removed under reduced pressure (to ca. 1 mL), and diethyl ether (20 mL) was added to precipitate a solid, which was filtered off, washed with

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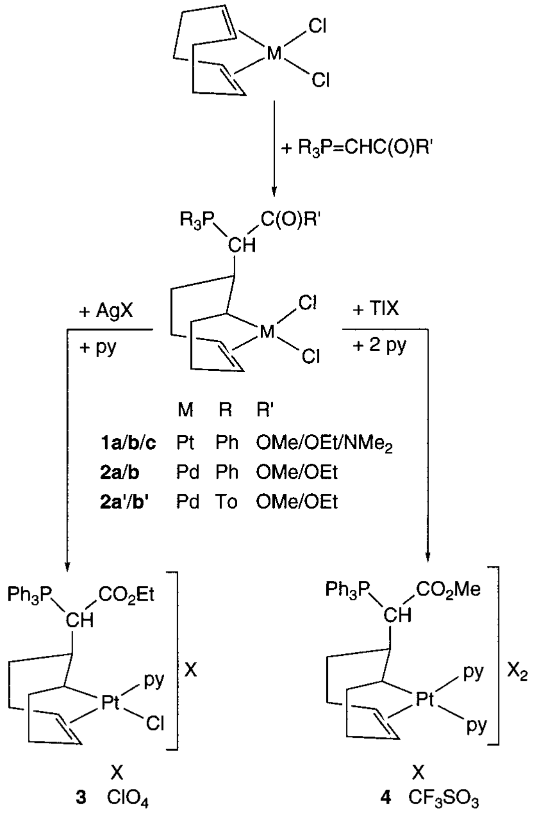
Scheme 1



diethyl ether (5 mL), and suction dried to give **3** as an off-white solid. Yield: 115 mg, 0.126 mmol, 61%. Mp: 113 °C. Anal. Calcd for $C_{35}H_{38}Cl_2NO_6PPt$: C, 48.56; H, 4.42; N, 1.62. Found: C, 48.24; H, 4.29; N, 1.50. ^1H NMR (300 MHz, $CDCl_3$): δ 1.07–2.31 (m, 8 H, H3, H4, H7, H8), 1.13 ("t", 3 H, CH_2*Me*), 2.74 (m, 1 H, H2), 3.14 (d, 1 H, H1), 4.05 (m, 2 H, C*H*$_2$Me), 4.27 (m, 1 H, H5), 4.48 (m, 1 H, H6), 4.54 (d, 1 H, C*H*, $^2J_{HP} = 12.0$ Hz), 7.43 (m, 1 H, *p*-py), 7.70–7.89 (m, 17 H, Ph, *m*-py), 8.54 (d, 2 H, *o*-py, $^3J_{HH} = 5.1$ Hz). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 20.75 (s). FAB MS: *m*/*z* (% abundance): 765 (M^+, 5), 687 ($M^+ -$ py, 76), 455 ($M^+ -$ Pt $-$ Cl $-$ py, 30), 348 [$CH(PPh_3)CO_2Et$, 15.6], 303 [Pt(COD), 100]. IR (cm^{-1}) ν(CO): 1720.

Synthesis of [Pt{C_8H_{12}{$CH(PPh_3)CO_2Me$}(py)$_2$](CF_3SO_3)$_2$ (4). Thallium triflate (306 mg, 0.667 mmol) was added to a stirring solution of **1a** (200 mg, 0.333 mmol) in dichloromethane (50 mL) and the reaction mixture left to stir for 2 h. Upon addition of pyridine (py) (44 mg, 0.667 mmol), the color of the solution changed from pale yellow to colorless. After 2 h, the mixture was filtered over $MgSO_4$ and then concentrated under reduced pressure (to ca. 1 mL). Diethyl ether (20 mL) was added, precipitating a solid, which was filtered off and then washed with diethyl ether to give **4** as a white solid. Crystals of **4** suitable for X-ray diffraction were grown from a 1:2 mixture of CH_2Cl_2 and diethyl ether. Yield: 0.231 mg, 0.212 mmol, 64%. Mp: 119 °C. Anal. Calcd for $C_{41}H_{41}F_6N_2O_8PPtS_2$: C, 45.02; H, 3.78; N, 2.56; S, 5.86. Found: C, 44.68; H, 3.81; N, 2.61; S, 5.73. NMR (300 MHz, $CDCl_3$, δ): ^1H, 1.31–2.29 (m, 8 H, H3, H4, H7, H8), 2.76 [m, 1H, H(2)], 3.18 [d, 1 H, H(1)], 3.60 [s, 3 H, Me], 4.23 [m, 1 H, H(5)], 4.42 [m, 1 H, H(6)], 4.66 [d, 1 H, C*H*, $^2J_{HP} = 11.7$ Hz], 7.56 [t, 1 H, *p*-py, $^3J_{HH} =$ 6.3 Hz]**,** 7.62–7.91 [m, 17 H, Ph, *m*-py], 8.54 [d, 2 H, *o*-py, $^3J_{HH}$ = 4.43 Hz]; $^{31}P\{^1H\}$, 19.23 (s). IR (cm^{-1}) ν(CO): 1724.

X-ray Structure Determinations. The crystals were mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment) as summarized in Table 1. The structures were solved by the heavy atom method and refined anisotropically on F^2 (program SHELX-93, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included using a riding model.

Table 1. Crystal Data for Compounds 1a·3$CDCl_3$ and 4

	1a·3$CDCl_3$	**4**
mol formula	$C_{32}H_{31}D_3Cl_{11}O_2PPt$	$C_{41}H_{41}F_6N_2O_8PPtS_2$
mol wt	1069.60	1093.94
wavelength (Å)	0.71073	0.71073
temp (K)	173(2)	173(2)
cryst size, mm	0.60 × 0.26 × 0.24	0.40 × 0.36 × 0.15
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/n$
a, Å	17.7921(13)	15.8478(12)
b, Å	18.398(2)	12.6315(8)
c, Å	25.016(2)	21.8574(12)
α, deg	90	90
β, deg	90	102.980(4)
γ, deg	90	90
volume (Å^3), *Z*	8188.7(11), 8	4263.6(5), 4
ρ(calc) (Mg m^{-3})	1.735	1.704
F(000)	4176	2176
μ, mm^{-1}	4.213	3.507
θ range for data collection (deg)	3.02–25.00	3.02–25.00
limiting indices	$0 \le h \le 21$, $-21 \le k \le 21$, $-29 \le l \le 0$	$-18 \le h \le 18$, $0 \le k \le 15$, $-25 \le l \le 25$
no. of reflns collected	7582	14976
no. of ind reflns	7187 ($R_{int} = 0.0365$)	7495 ($R_{int} = 0.0680$)
abs corr	ψ-scans	ψ-scans
max. and min. transmission	0.9420 and 0.6380	0.87112 and 0.64259
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	7187/322/419	7495/822/592
goodness-of-fit on F^2	1.036	0.982
R1[a]	0.0613	0.0437
wR2[b]	0.1509	0.1087
largest diff peak and hole (e Å^{-3})	1.579 and −2.615	1.281 and −1.085

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\,]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

For compound **1a**·3$CDCl_3$ unit cell parameters were determined from a least-squares fit of 64 accurately centered reflections ($10.1 < 2\theta < 25.8$). Maximum $\Delta/\sigma = 0.001$, maximum $\Delta\rho = 1.58$ e Å^{-3}.

For compound **4** unit cell parameters were determined from a least-squares fit of 62 accurately centered reflections ($9.7 < 2\theta < 25.0$). The two triflate molecules corresponding to C98 and C99 are disordered over two sites (61/39% and 77/23% occupancy). Maximum $\Delta/\sigma = 0.001$, maximum $\Delta\rho = 1.28$ e Å^{-3}.

The programs use the neutral atom scattering factors, $\Delta f'$ and $\Delta f''$, and absorption coefficients from International Tables for Crystallography.[24] Figures 1 and 2 show ellipsoid representations, Table 1 shows crystallographic data, and Tables 2 and 3 show selected bond lengths and angles for complexes **1a** and **4**.

Results and Discussion

Synthesis. Complexes [MCl_2{C_8H_{12}{$CH(PR_3)C(O)$-R'}}] [M = Pt, R = Ph, R' = OMe (**1a**), OEt (**1b**), NMe_2 (**1c**); M = Pd, R = Ph, R' = OMe (**2a**), OEt (**2b**), R = To, R' = OMe(**2a'**), OEt (**2b'**)] were synthesized by reacting equimolar amounts of [MCl_2(COD)] (M = Pt, Pd; COD

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[24] *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4 (pp 500–502), 4.2.6.8 (pp 219–222), and 4.2.4.2 (pp 193–199).

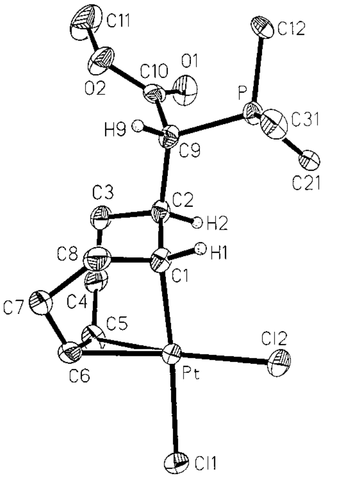

Figure 1. Ellipsoid representation of **1a**·3$CDCl_3$ with 50% probability ellipsoids and the labeling scheme. The H atoms on achiral carbon atoms, the aryl groups (except the *ipso* carbons), and the solvent are omitted for clarity.

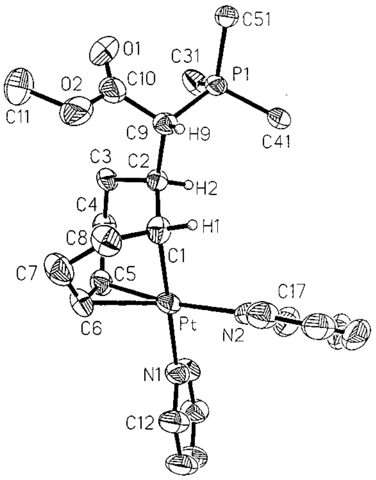

Figure 2. Ellipsoid representation of the cation of **4** with 50% probability ellipsoids and the labeling scheme. The H atoms on achiral carbon atoms and the aryl groups (except the *ipso* carbons) are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 1a

Pt−C(1)	2.051(9)	Pt−C(6)	2.096(11)
Pt−C(5)	2.153(10)	Pt−Cl(2)	2.333(2)
Pt−Cl(1)	2.440(2)	P−C(9)	1.834(10)
C(1)−C(2)	1.517(13)	C(1)−C(8)	1.539(13)
C(2)−C(3)	1.537(12)	C(3)−C(4)	1.525(14)
C(4)−C(5)	1.49(2)	C(5)−C(6)	1.40(2)
C(6)−C(7)	1.53(2)	C(7)−C(8)	1.54(2)
C(1)−Pt−C(6)	82.4(4)	C(1)−Pt−C(5)	88.4(4)
C(1)−Pt−Cl(2)	92.8(3)	C(6)−Pt−Cl(1)	93.7(3)
C(5)−Pt−Cl(1)	89.4(3)	Cl(2)−Pt−Cl(1)	90.29(10)
C(6)−C(5)−C(4)	129.4(11)	C(5)−C(6)−C(7)	125.3(10)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

Pt−C(1)	2.057(7)	Pt−C(6)	2.144(7)
Pt−C(5)	2.140(6)	Pt−N(2)	2.057(6)
Pt−N(1)	2.151(6)	P1−C(9)	1.837(7)
C(1)−C(2)	1.546 (9)	C(1)−C(8)	1.532(10)
C(2)−C(3)	1.550(8)	C(3)−C(4)	1.514(10)
C(4)−C(5)	1.504(10)	C(5)−C(6)	1.393(9)
C(6)−C(7)	1.503(11)	C(7)−C(8)	1.528(11)
C(1)−Pt−C(6)	81.7(3)	C(1)−Pt−C(5)	90.5(3)
C(1)−Pt−N(2)	91.8(2)	C(6)−Pt−N(1)	97.6(3)
C(5)−Pt−N(1)	89.4(2)	N(2)−Pt−N(1)	88.6(2)
C(6)−C(5)−C(4)	129.4(7)	C(5)−C(6)−C(7)	128.1(7)

= C_8H_{12} = 1,5-cyclooctadiene) and the appropriate ylide $R_3P{=}CHC(O)R'$ (R = Ph, PhMe-4; R′ = OMe, OEt, NMe_2) in acetone or dichloromethane solution. It is noticeable that the reactions take place under mild conditions (room temperature, 4−24 h) despite the low nucleophilicity of the carbonyl-stabilized phosphorus ylides. Under similar reaction conditions, the less basic ylide $Ph_3P{=}CHC(O)Ph$ does not react with $[MCl_2(COD)]$ (M = Pd, Pt). Complex **1c** could only be obtained using acetone, as the reaction of $[PtCl_2(COD)]$ with $Ph_3P{=}CHC(O)NMe_2$ in dichloromethane gave a mixture from which we were unable to isolate a cyclooctenyl complex. Similarly, the reaction of $[PdCl_2(COD)]$ with $Ph_3P{=}CHC(O)NMe_2$ in dichloromethane gave a mixture from which the only identified product was a small amount of $\{Ph_3PCH_2C(O)NMe_2\}_2[PdCl_4]$, which could be attributed to the presence of traces of HCl in the solvent resulting from its decomposition. The reaction of $[PtCl_2(COD)]$ with $R_3P{=}CHCO_2Me$ in 1:2 molar ratio gave complex **1a,** and half of the used ylide was recovered from the mother liquor.

Complex $[PtCl\{C_8H_{12}\{CH(PPh_3)CO_2Et\}(py)]ClO_4$ (**3**) was formed by removing a chloro ligand from complex **1** by the addition of the equimolar amount of silver perchlorate, followed by filtration and then the addition of 1 equiv of pyridine to the filtrate. Similarly, $[Pt\{C_8H_{12}\{CH(PPh_3)CO_2Me\}(py)_2](CF_3SO_3)_2$ (**4**) was obtained from **1**, $Tl(CF_3SO_3)$, and pyridine in 1:2:2 molar ratio.

The platinum complexes **1**, **3**, and **4** are white solids, while the palladium derivatives **2** are pale yellow. They are all air-stable solids soluble in dichloromethane and chloroform, partially soluble in acetone, and insoluble in diethyl ether or *n*-hexane.

All attempts to prepare metalated ylides of the type $[M]\{C_8H_{12}\{C({=}PR_3)C(O)R'\}\}$ by deprotonation of the cyclooctenyl complexes here described failed. The reactions of the neutral (**1, 2**) or cationic (**3, 4**) complexes with bases such as NaOH or Na_2CO_3 gave yellow oils from which we could not isolate any pure compound.

The reactions of the ylide Ph_3PCHCO_2Me with the cationic complexes $[Pd(COD)(acac)]BF_4$ (acac = acetylacetonate) and $[Pd(COD)(C_5H_5)]BF_4$, which were intended to produce new cyclooctenyl complexes, caused decomposition. On the other hand, the reactions of complexes **1a**−**c** with $Tl(CF_3SO_3)$ and $Tl(C_5H_5)$ (1:1:1) produced $[Pt(COD)(C_5H_5)]CF_3SO_3$.

X-ray Crystal Structures of 1a and 4. The structures of complexes **1a** and **4** display many common features: (i) they show the platinum in a distorted square planar environment coordinated to an alkyl carbon atom [C(1)], an olefinic [C(5)=C(6)] bond, and two chloro (**1a**) or two pyridine (**4**) ligands in mutually *cis* disposition; (ii) the attack of the ylide on the 1,5-cyclooctadiene ligand is produced in an *exo* fashion to give cyclooctenyl complexes with three chiral centers, C(1), C(2), and C(9) (see Figures 1 and 2); (iii) the cyclooctenyl carbon atom bonded to platinum [C(1)] and the phosphonium carbon atom [C(9)] display the same chirality, opposite to that of the cyclooctenyl carbon atom attacked by the ylide [C(2)]; (iv) the P−C(9) bond distances [1.834(10) (**1a**), 1.837(7) Å (**4**)] are normal for

Table 4. NMR and IR Data for Phosphonium Salts, Phosphorus Ylides, and Complexes 1−4

compound	NMR (δ)		IR (cm^{-1})
	^{1}H (CH$_2$/CH)	^{31}P	ν(CO)
[$Ph_3PCH_2CO_2Me$]Cl	5.50 (d)	20.7	1720
Ph_3PCHCO_2Me	2.82 (br)	15.3	1618
[$PtCl_2\{C_8H_{12}\{CH(PPh_3)CO_2Me\}\}$] (**1a**)	4.45 (d)	24.2	1724
[$PdCl_2\{C_8H_{12}\{CH(PPh_3)CO_2Me\}\}$] (**2a**)	4.59 (d)	23.7	1720
[$Pt\{C_8H_{12}\{CH(PPh_3)CO_2Me\}(py)_2\}$]($CF_3SO_3$)$_2$ (**4**)	4.66 (d)	19.2	1734
[$To_3PCH_2CO_2Me$]Cl^a	5.44 (d)	19.6	1720
To_3PCHCO_2Me	2.89 (br)	18.2	1637
[$PdCl_2\{C_8H_{12}\{CH(PTo_3)CO_2Me\}\}$] (**2a′**)	4.40 (d)	22.9	1714
[$Ph_3PCH_2CO_2Et$]Cl	5.40 (d)	21.1	1720
Ph_3PCHCO_2Et	2.85 (br)	17.9	1614
[$PtCl_2\{C_8H_{12}\{CH(PPh_3)CO_2Et\}\}$] (**1b**)	4.43	24.3	1718
[$PdCl_2\{C_8H_{12}\{CH(PPh_3)CO_2Et\}\}$] (**2b**)	4.52	23.7	1720
[$PtCl\{C_8H_{12}\{CH(PPh_3)CO_2Et\}(py)\}$]$ClO_4$ (**3**)	4.54	20.7	1720
[$To_3PCH_2CO_2Et$]Cl	5.46 (d)		1720
To_3PCHCO_2Et	2.89 (br)	15.3	1612
[$PdCl_2\{C_8H_{12}\{CH(PTo_3)CO_2Et\}\}$] (**2b′**)	4.40	22.9	1706
[$Ph_3PCH_2C(O)NMe_2$]Cl	5.54 (d)	21.7	1630
$Ph_3PCHC(O)NMe_2$	2.80	17.3	1530
[$PtCl_2\{C_8H_{12}\{CH(PPh_3)C(O)NMe_2\}\}$] (**1c**)	4.90 (d)	24.9	1634

[a] To = C_6H_4Me-4.

C(sp^3)−P single bonds in phosphonium salts,[25] while the C(10)−O(1) [1.179(12) (**1a**), 1.192(10) Å (**4**)] bond distances are similar to the typical values found[25] for C(sp^2)=O double bonds in esters and amides, respectively. Both distances are similar to their analogues found in some complexes derived from the ylides $Ph_3P=CHC(O)OEt$[26] and $Ph_3P=CHC(O)NMe_2$,[27] respectively, and (v) according to the greater *trans* influence of σ-carbon donor ligands with respect to olefins, the Pt−Cl(1) bond distances in **1a** [2.440(2) Å] or the Pt−N(1) bond distance in **4** [2.151(6) Å] *trans* to C(1) is longer than the corresponding Pt−Cl(2) distances [2.333(2) Å (**1a**)] or Pt−N(2) [2.057(6) Å (**4**)] *trans* to the C(5)=C(6) double bond.

NMR Spectra. The ^{1}H NMR spectra of complexes **1**−**4** show the resonance due to the CH proton as a doublet due to coupling to the phosporus atom in α-position. The $^2J_{PH}$ coupling constants range from 11.7 (**2a**) to 12.4 (**1c**) Hz, these values being similar to those observed for the corresponding phosphonium chlorides (see Table 4). In all cases the CH resonance is intermediate between that of the corresponding ylide and phosphonium chloride, although closer to the values observed for the phosphonium salts. A slight downfield shift is observed for the CH resonance in the palladium complexes **2a, b** (4.59 and 4.52 ppm, respectively) with respect to that in the homologous platinum derivatives **1a, b** (4.45 and 4.43 ppm, respectively). The moderately increasing values found for this resonance in the family of platinum complexes [$Ptl\{C_8H_{12}\{CH(PPh_3)CO_2Et\}LL'\}$]$^{n+}$ [4.43 (L = L′ = Cl, n = 0, **1b**) < 4.54 (L = Cl, L′ = py, n = 1, **3**) < 4.66 (L = L′ = py, n = 2, **4**) ppm] could be due to the enhancement of the electronegativity of the Pt moiety with the increasing positive charge of the complex.

Each spectrum also displays two clear multiplets for the vinyl protons of the cyclooctenyl ligand. In the palladium complexes these are downfield from those of the platinum analogues.

The ring hydrogens of the cycloctenyl ligand give rise to a complex series of overlapping multiplets in the 1.02−2.32 ppm region. These were assigned with the help of ^{1}H−^{1}H 2D COSY NMR experiments. In all complexes, the resonance due to the proton α to the metal (H$_1$) is a doublet appearing in the 3.21−3.32 (Pt) or 3.86−3.95 (Pd) ppm region with $^3J_{HH}$ coupling constants lying in the narrow range 5.7−6.3 Hz. In a very recent paper Anderson et al.[5] have found that similar appearance and coupling constants for the H$_1$ resonance in a series of [$Pd\{C_8H_{12}$(nucleophile)$\}$] complexes are indicative of similar stereochemistry. According to this and the crystal structures of **1a** and **4**, we assume all the complexes here reported to be the *exo* isomers.

In complexes **1b**, **2b**, **2b′**, and **3** containing the $\{C_8H_{12}\{CH(PR_3)CO_2Et\}$ moiety the Et group is an ABX$_3$ system due to the presence of the three chiral centers. However, the X$_3$ component is an apparent triplet in the 1.10−1.14 ppm range, presumably because $(J_{AX} - J_{BX})/J_{AB} \approx 0$. The AB component, which should be composed of four AB subspectra (1:3:3:1), is observed in all cases as a multiplet in the 3.80−4.10 ppm range, complicated in complex **2b** due to the superimposition of the resonance due to the cyclooctenyl proton H1.

The ^{1}H NMR spectrum of complex **1c** containing the dimethylcarbamoyl moiety shows both Me groups attached to the nitrogen atom to be inequivalent. While in the ylide $Ph_3PCHC(O)NMe_2$ both Me groups are equivalent [2.92 (s) ppm], we have observed inequivalent Me groups in the parent phosphonium salts [$Ph_3PCH_2C(O)NMe_2$]X [X = Cl, 2.69 (s), 3.25 (s); X = ClO$_4$, 2.82 (s), 3.16 (s) ppm] and also in some silver(I) and gold(I) complexes of the type [M]−$\{CH(PPh_3)C(O)NMe_2\}$.[27] This could be attributed to the contribution of a resonance form with the CN double bond increasing the energy for the free rotation of the NMe$_2$ group.

Further evidence for the conversion of the phosphorus ylide to a phosphonium salt upon attack of the 1,5-cyclooctadiene complexes of palladium or platinum comes from the ^{31}P$\{^1$H$\}$ NMR spectroscopic data. Table

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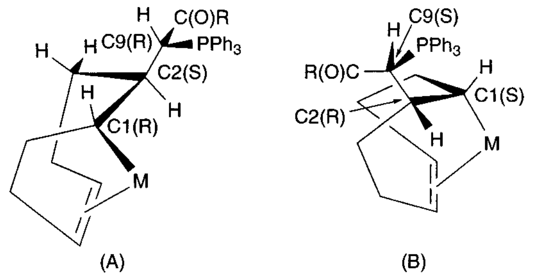
[25] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 1* **1987**, S1.

[26] Vicente, J.; Chicote, M. T.; Cayuelas, J. A.; Fernández-Baeza, J.; Jones, P. G.; Sheldrick, G. M.; Espinet, P. *J. Chem. Soc., Dalton Trans.* **1985**, 1163.

[27] Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1991**, 2579.

Chart 2



4 shows the ^{31}P{^{1}H} NMR chemical shifts for a range of phosphorus ylides and phosphonium salts. It can be seen that complexes **1**−**4** give rise to signals shifted significantly downfield from those of the corresponding ylides and closer to the values observed for the phosphonium salts.

Each of the complexes here reported display three chiral carbon atoms, C1, C2, and C9. The attack of the ylide on the 1,5-cyclooctadiene complex causes opposite chirality on the carbon atoms of the attacked olefin, C1 and C2, which can adopt RS or SR conformation (Chart 2). These, along with the two possible conformations of C9, leave up to four possible isomers displaying the C(1)C(2)C(9) sequences RSR, RSS, SRR, and SRS. However, according to the NMR studies, only the enantiomer couple RSR (A) and SRS (B) or RSS and SRR must form. The X-ray diffraction studies on **1a** and **4** show that the ylide carbon atom (C9) adopts a chirality opposite that of the carbon atom to which it is bonded (C2). Therefore, the pair of enantiomers A and B in Chart 2 are the products of the nucleophilic attack. This stereospecificity could reasonably be attributed to steric reasons.

IR Spectra. The IR spectra of complexes **1**−**4** all show an intense absorption at 1634 (**1c**) to 1724 (**4**) cm^{-1} assignable to the $\nu_{\rm assym}$(CO$_2$) [or ν(CO) in **1c**] stretching mode. In all cases this band is shifted to the higher wavenumber region with respect to that in the corresponding free ylide between 77 (**2a′**) and 106 (**4**) cm^{-1}. We have previously attributed a similar blue-shift found in many silver (I),[27,28] gold (I),[26,27,29−39] gold(III),[26,27,29−31] and palladium (II)[40−43] ylide complexes to the reinforcement of the p(π)O → p(π)C bond component caused by the nucleophilic attack of the ylide at the metal center, and the same argument could be also used in this case. We have previously shown that in complexes containing carbonyl-stabilized phosphorus ylide moieties there is a close dependence of the position of the CO band on the electronegativity of the substituents attached to the ylide carbon atom.[29] In this context, the position of this band in each of the complexes described here, being very close to the analogous band in the corresponding phosphonium salt, is indicative of the similar electron-withdrawing ability of the [M{C$_8$H$_{12}${CH(PR$_3$)C(O)R′] [M = Pd, Pt, R = Ph, To, R′ = OMe, OEt, NMe$_2$] moieties with respect to that of the proton.

Complexes **1** and **2** show one or two bands between 260 cm^{-1} and the lower limit of our spectrophotometer (200 cm^{-1}) that can tentatively be assigned to ν(M−Cl). In particular, complex **1b** shows a medium-intensity band at 250 cm^{-1} that could be due to ν(M−Cl) *trans* to the olefin bond, while that corresponding to ν(M−Cl) *trans* to the σ-bonded carbon atom could be below 200 cm^{-1} due to the greater *trans* influence of the latter (see the X-ray data discussion). The fact that for complex **3** the above-mentioned 250 cm^{-1} band is absent suggests the chloro ligand to be *trans* to the σ-bonded carbon atom.

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Supporting Information Available: A listing of all both refined and calculated atomic coordinates, all the anisotropic thermal parameters, and full bond lengths and angles for compounds **1a**·3CDCl$_3$ and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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