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Nucleophilic Attack of Carbonyl-Stabilized Phosphorus Ylides on Neutral and Cationic Alkene Platinum(II) Complexes

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The carbonyl-stabilized phosphorus ylides $Ph_3P{=}CHCO_2R$ (R = Me, Et) react with the platinum complexes $[PtCl(\eta^2\text{-}CH_2{=}CH_2)(N,N,N',N'\text{-tetramethylethylenediamine})]ClO_4$ and $[PtCl_2(\eta^4\text{-diene})]$ (diene = 1,5-hexadiene (C_6H_{10}), dicyclopentadiene ($C_{10}H_{12}$), 4-vinylcyclohex-1-ene (C_8H_{12}), norbornadiene (C_7H_8)) to give complexes resulting from nucleophilic attack of the ylide at one of the olefinic carbons. The crystal structures of $[PtCl_2\{\eta^3\text{-}C_6H_{10}CH(PPh_3)CO_2Et\}]$, $[PtCl_2\{\eta^3\text{-}C_{10}H_{12}CH(PPh_3)CO_2Me\}]\cdot 0.5CH_2Cl_2$, and $[PtCl_2\{\eta^3\text{-}C_8H_{12}CH(PPh_3)CO_2Me\}]\cdot 2CHCl_3$ are reported and indicate an exo attack in the case of the dicyclopentadiene complex and anti-Markovnikov addition (attack at the CH_2 group) in the other two complexes.

Introduction

Although phosphorus ylides have been shown to function as ligands with virtually every metal of the periodic table,[1] their use as nucleophiles toward coordinated ligands has been scarcely examined. Thus, the complexes $[Fe(\eta^5\text{-}Cp)(CO)(L)(\eta^2{-}CH_2{=}CH_2)]$ (L = CO, PPh_3) react with $Ph_3P{=}CHR$ (R = H,[2] CO_2Me,[3] respectively) to give $[Fe(\eta^5\text{-}Cp)(CO)(L)\{CH_2CH_2CHR(PPh_3)\}]$. Similarly, the cluster $[FeCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)]$ reacts with $Ph_3P{=}CHR$ (R = H, CO_2Et, C(O)Ph, $SiMe_3$) to give $[FeCo_2(CO)_9\{\mu_3\text{-}CCH_2CHR(PPh_3)\}]$.[4]

We have reported[5] that reactions of $[PtCl_2(NCPh)_2]$ with carbonyl-stabilized phosphorus ylides $Ph_3P{=}CHCO_2R$ (R = Me, Et) did not give the expected ylide complexes $[PtCl_2\{CH(PPh_3)CO_2R\}_2]$. Instead, complexes of the type $[PtCl_2\{N({=}PPh_3)C(Ph){=}CHCO_2R\}(NCPh)]$ were obtained that contain an iminophosphorane ligand resulting from the nucleophilic attack of the ylide on one of the benzonitrile ligands. This opened further research, leading to the synthesis of a range of platinum(II) complexes containing N-bonded iminophosphorane and/or N-bonded β-iminophosphorus ylide ligands.[6] These results could not be extended to $[PtCl_4(NCMe)_2]$ because reduction to $[PtCl_2(NCMe)_2]$ was observed when the ylide $Ph_3P{=}CHCO_2Me$ was used.[7]

Recently, we described[8] the reactions of carbonyl-stabilized phosphorus ylides with the complexes $[MCl_2(\eta^4\text{-cod})]$ (M = Pt, Pd; cod = 1,5-cyclooctadiene). Again, instead of the expected $[MCl_2\{CH(PR_3)CO_2R\}_2]$, complexes were obtained resulting from the nucleophilic attack of the ylide on the cod ligand. In this paper, we extend this study to the reactivity of ylides $Ph_3P{=}CHCO_2R$ (R = Me, Et) toward other $[PtCl_2(\eta^4\text{-diene})]$ complexes and toward the cationic complex $[PtCl(\eta^2\text{-}CH_2{=}CH_2)(tmeda)]ClO_4$ (tmeda = N,N,N′,N′-tetramethylethylenediamine). One of our objectives was to study the regio- and stereoselectivity of these reactions, and for this reason we chose complexes with different diolefins such as 1,5-hexadiene, dicyclopentadiene, 4-vinylcyclohex-1-ene, and norbornadiene.

The nucleophilic attack on alkenes coordinated to platinum(II) is very well documented,[9−11] and nucleophiles such as hydroxide, alkoxide,[12−16] nitro,[12] acetylacetonate,[12,17−19] ammonia and amines,[19−27] ethyl acetoace-

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tate, diethyl malonate,[17,19,28] carboxylate,[13] azide,[11,29] cyanate,[29,30] cyclopentadienyl,[31] 1,8-bis(dimethylamino)-naphthalene (Proton Sponge),[32] and chloride[33] have been studied. Some of these processes have been of utility in organic synthesis.[33,34] In most cases, these reactions took place in an exo fashion; i.e., the nucleophile directly attacks at the coordinated double bond, giving complexes in which it is anti with respect to the metal. The endo mode is less common; it occurs when the coordination of the nucleophile precedes a migratory insertion of the double bond into the M−nucleophile bond.[31,35] Despite the great number of products obtained through these nucleophilic additions and the different isomers that can be obtained in some of these reactions (exo or endo, Markovnikov or anti-Markovnikov), only two crystal structures have been reported.[20,30] Curiously, they are derivatives of ethylene platinum complexes which can only give one type of addition product. We have reported the crystal structure of the complex that we obtained in the reaction between $[PtCl_2(\eta^4\text{-cod})]$ and $Ph_3P{=}CHCO_2Me$, showing that the attack of the ylide on the cod took place in an exo fashion.[8] In this paper we report three crystal structures showing the mode of attack of the ylides studied toward some other dienes. Another objective of the present work was to check the generality of the above-mentioned behavior. In view of the facile coordination of ylides to platinum,[36] we thought it possible that in $[PtCl_2(\eta^4\text{-diene})]$ complexes, other than $[PtCl_2(\eta^4\text{-cod})]$, coordination could be preferred to the direct nucleophilic attack on the alkene, resulting, in this case, in complexes $[PtCl_2\{CH(PR_3)CO_2R\}_2]$ or those resulting after an endo attack.

Experimental Section

The IR spectra, elemental analyses, and melting point determinations were carried out as described earlier.[37] Unless otherwise stated, the reactions were conducted at room temperature without special precautions against moisture. Technical grade solvents were purified by standard procedures. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded with Varian Unity 300 or Bruker AC-200 spectrometers, and chemical shifts, given in ppm, are referred to TMS (^1H) or H_3PO_4 ($^{31}P\{^1H\}$). $[PtCl(C_2H_4)(tmeda)]ClO_4$ was prepared according to the literature procedure.[38] The $[PtCl_2(diene)]$ complexes were prepared via the displacement of benzonitrile ligands from $[PtCl_2(NCPh)_2]$ (thf, reflux, 5 h).[14−16,39,40]

Synthesis of $[PtCl\{CH_2CH_2CH(PPh_3)CO_2Me\}(tmeda)]ClO_4$ (1). The ylide $Ph_3P{=}CHCO_2Me$ (0.067 g, 0.200 mmol) was added to a rapidly stirred solution of $[PtCl(\eta^2\text{-}CH_2{=}CH_2)(tmeda)]ClO_4$ (0.100 g, 0.200 mmol; tmeda = *N,N,N′,N′*-tetramethylethylenediamine) in Me_2CO (50 mL), and the reaction mixture was stirred further for 24 h. The resulting solution was concentrated to ca. 2 mL; addition of Et_2O (25 mL) then gave a precipitate that was washed with Et_2O to give **1** as a white solid (0.124 g, 0.153 mmol). Yield: 77%. Mp: 151 °C. Anal. Calcd for $C_{29}H_{39}Cl_2N_2O_6PPt$: C, 43.08; H, 4.86; N, 3.46. Found: C, 43.42; H, 4.73; N, 3.75. ^1H NMR (200 MHz, $CDCl_3$): δ 1.41−2.59 (m, 4 H, CH_2CH_2), 2.69 (s, 3 H, NMe), 2.73 (s, 3 H, NMe), 2.76 (s, 3 H, NMe), 2.85 (s, 3 H, NMe), 3.50 (s, 3 H, OMe), 4.89 (m, 1 H, CHP), 7.65−7.87 (m, 15 H, Ph). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 24.08 (s). FAB MS (*m/z* (%, abundance)): 709 ($M^+ - ClO_4$, 89), 363 ($CH_2CH_2CH(PPh_3)CO_2Me$, 100). IR (cm^{-1}; ν(CO)): 1728.

Synthesis of $[PtCl_2\{\eta^3\text{-}C_6H_{10}CH(PPh_3)CO_2R\}]$ (R = Me (2a), Et (2b)), $[PtCl_2\{\eta^3\text{-}C_{10}H_{12}CH(PPh_3)CO_2Me\}]$ (3), $[PtCl_2\{\eta^3\text{-}C_8H_{12}CH(PPh_3)CO_2Me\}]$ (4), and $[PtCl_2\{\eta^3\text{-}C_7H_8CH(PPh_3)CO_2Me\}]$ (5). To a rapidly stirred solution of the appropriate $[PtCl_2(\eta^4\text{-diene})]$ complex (ca. 0.5 mmol) in 30 mL

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of Me_2CO (CH_2Cl_2 for **5**) was added an equimolar amount of the ylide $Ph_3P{=}CHCO_2R$. The reaction mixture was stirred further for 24 h, during which time a white precipitate formed. The resulting suspension was concentrated to ca. 2 mL, whereupon the addition of Et_2O (25 mL) completed the precipitation of complexes **2**−**5** as white solids that were washed with Et_2O (2 × 5 mL) and suction-dried.

2a. Yield: 78%. Mp: 194 °C. Anal. Calcd for $C_{27}H_{29}Cl_2O_2PPt$: C, 47.52; H, 4.28. Found: C, 47.54; H, 4.10. ^1H NMR (200 MHz, $CDCl_3$): δ 0.8−3.2 (several m, 8 H, $CH_2CH(Pt)CH_2CH_2CH$), 3.71 (s, 3 H, OMe), 3.86 (m, 1 H, $=CH_2$), 4.5 (m, 1 H, CHP), 5.98 (m, 1 H, $=CH_2$), 7.67−7.92 (m, 15 H, Ph). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ 26.74 (s). IR (cm^{-1}; ν(CO)): 1724.

2b. Yield: 73%. Mp: 182 °C. Anal. Calcd for $C_{28}H_{31}Cl_2O_2PPt$: C, 48.28; H, 4.49. Found: C, 48.24; H, 4.33. ^1H NMR (300 MHz, $CDCl_3$): δ 0.97 (t, 3 H, Me), 1.24−2.87 (several m, 8 H, $CH_2CH(Pt)CH_2CH_2CH$), 3.83 (m, 1 H, $=CH_2$), 3.94 (m, 2 H, CH_2Me), 4.65 (m, 1 H, CHP), 6.11 (m, 1 H, $=CH_2$), 7.68−7.91 (m, 15 H, Ph). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): 26.81 (s). IR (cm^{-1}; ν(CO)): 1722.

3. Yield: 80%. Mp: 180 °C. Anal. Calcd for $C_{31}H_{31}Cl_2O_2PPt$: C, 50.83; H, 4.27. Found: C, 50.44; H, 4.33. ^1H NMR (200 MHz, $CDCl_3$): δ 1.0−3.0 (several m, 10 H), 3.48 (s, 3 H, OMe), 4.67 (m, 1 H, CHP), 4.86 (m, 1 H, $=CH_2$), 5.83 (m, 1 H, $=CH_2$), 7.66−7.94 (m, 15H, Ph). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 22.86 (s). IR (cm^{-1}; ν(CO)): 1728.

4. Yield: 68%. Mp: 142 °C. Anal. Calcd for $C_{29}H_{31}Cl_2O_2PPt$: C, 49.16; H, 4.41. Found: C, 49.44; H, 4.30. ^1H NMR (300 MHz, $CDCl_3$): δ 0.8−3.56, 3.60−5.60 (several m, 13 H), 3.57 (s, 3 H, OMe), 7.66−7.90 (m, 15 H, Ph). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 26.88 (s). IR (cm^{-1}; ν(CO)): 1728.

5. Yield: 66%. Mp: 194 °C. Anal. Calcd for $C_{28}H_{27}Cl_2O_2PPt$: C, 48.57; H, 3.93. Found: C, 48.23; H, 3.83. ^1H NMR (300 MHz, $CDCl_3$): δ 1.35−3.40 (several m, 6 H), 3.48 (s, 3 H, OMe), 3.98 (m, 1 H, $=CH_2$), 4.7 (m, 1 H, CHP), 5.2 (m, 1 H, $=CH_2$), 7.4−7.9 (m, 15 H, Ph). $^{31}P\{^1H\}$ NMR (300 MHz, CD_2Cl_2): δ 24.42 (s). IR (cm^{-1}; ν(CO)): 1730.

X-ray Structure Determinations. Crystals of **2b**, **3**·$0.5CH_2Cl_2$, and **4**·$2CHCl_3$ suitable for X-ray diffraction studies were grown by the liquid diffusion method using CH_2Cl_2 (**2b**, **3**) or chloroform (**4**) and Et_2O. Data were collected on a Bruker SMART 1000 CCD diffractometer fitted with a low-temperature device. Structures were solved with the heavy-atom method and refined on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Göttingen, Germany). Hydrogen atoms of the coordinated olefin groups were located in difference syntheses and refined freely, but with C−H distance restraints. Other hydrogens were included using a riding model or rigid methyl groups. Special features of refinement are as follows. For all structures, light-atom *U* value components were restrained to be equal (command DELU). For **3** and **4**, the local ring geometry of phenyl groups was also restrained (FLAT, SAME). Structure **4** was refined as an enantiomeric twin. The solvent molecule in **3** is disordered over an inversion center. The two solvent molecules in **4** are well ordered. Crystal data are presented in Table 1.

Results and Discussion

Synthesis. The reaction in acetone of equimolar amounts of the complex $[PtCl(\eta^2\text{-}CH_2{=}CH_2)(tmeda)]ClO_4$ (tmeda = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine) and the ylide $Ph_3P{=}CHCO_2Me$ gave the complex $[PtCl\{CH_2CH_2CH(PPh_3)CO_2Me\}(tmeda)]ClO_4$ (**1**),) as shown in Scheme 1. Previous studies of nucleophilic attack on $[PtCl(\eta^2\text{-}CH_2{=}CH_2)(tmeda)]ClO_4$ have dealt mainly with anionic nucleophiles such as acetylacetone, ethyl acetatoacetate, and diethyl malonate in the presence of bases,[17] OH^-, RO^-, $MeCO_2^-$,[13] NO_2^-, N_3^-, CN^-,[29] and NCO^-.[29,30] There is only one exception: the reaction with 1,8-bis(dimethylamino)naphthalene (Proton Sponge) gives a product in which the $CH_2CH_2PtCl(tmeda)$ moiety has replaced the 4-proton of the nucleophile, which is taken up by the amino groups.[32] Therefore, in contrast to the current work, most of the resulting addition products were neutral complexes.

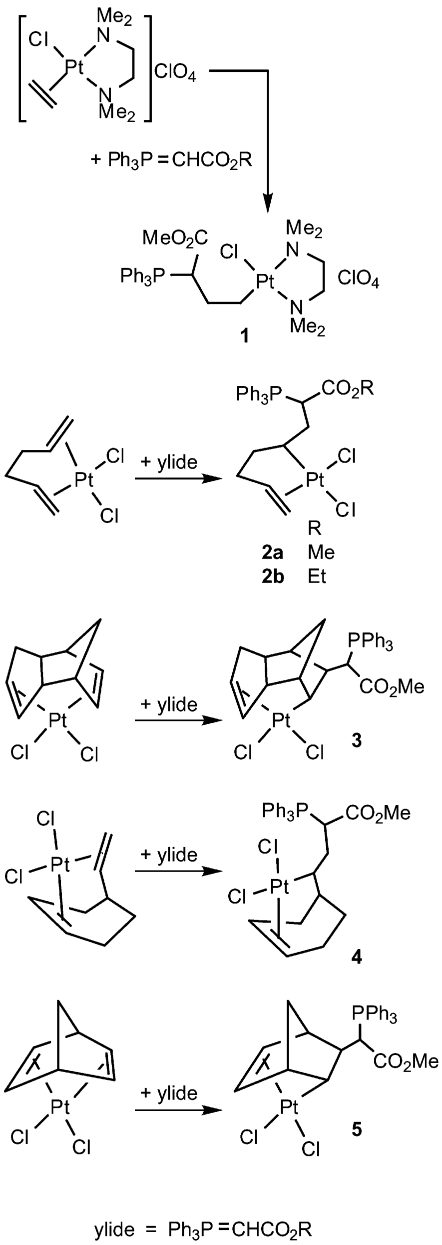
Table 1. Crystal Data for Compounds 2b, 3·0.5CH$_2$Cl$_2$, and 4·2CHCl$_3$

	2b	**3**·$0.5CH_2Cl_2$	**4**·$2CHCl_3$
formula	$C_{28}H_{31}Cl_2O_2PPt$	$C_{31.5}H_{32}Cl_3O_2PPt$	$C_{31}H_{33}Cl_8O_2PPt$
cryst habit	colorless prism	colorless prism	colorless tablet
cryst size (mm)	0.27 × 0.24 × 0.19	0.22 × 0.10 × 0.08	0.24 × 0.21 × 0.14
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	Pn
a (Å)	9.6743 (8)	11.7034(10)	12.1500(12)
b (Å)	11.8139 (10)	12.2222(10)	8.8305(8)
c (Å)	23.728(2)	12.6338(10)	16.9544(16)
α (deg)	90	110.224(3)	90
β (deg)	101.097(3)	101.911(3)	106.744(3)
γ (deg)	90	113.268(3)	90
V (Å^3)	2661.1(4)	1429(2)	1741.9(3)
Z	4	2	2
ρ_{calcd} (Mg m^{-3})	1.738	1.801	1.806
M_r	696.49	774.98	947.23
λ (Å)	0.710 73	0.710 73	0.710 73
T (K)	143(2)	143(2)	143(2)
F(000)	1368	762	928
μ(Mo Kα) (mm^{-1})	5.557	5.274	4.716
θ range (deg)	1.93−30.00	1.87−30.00	1.84−30.03
abs cor	SADABS	SADABS	SADABS
no. of rflns coll	21 762	17 137	20 811
no. of indep rflns	7750	8247	10 020
R_{int}	0.0253	0.0415	0.0529
transmissn	0.949/0.740	0.98/0.60	0.962/0.742
no. of data/restraints/params	7750/61/315	8247/104/351	10 020/277/398
R1 ($I > 2\sigma(I)$)	0.0233	0.0289	0.0295
wR2 (all rflns)	0.0523	0.0679	0.0523
max $\Delta\rho$ (e Å^{-3})	2.321	1.405	1.112
$S(F^2)$	0.978	1.007	0.924

The complexes $[PtCl_2(\eta^4\text{-diene})]$ (diene = 1,5-hexadiene (C_6H_{10}), dicyclopentadiene ($C_{10}H_{12}$), 4-vinylcyclohex-1-ene (C_8H_{12}), norbornadiene (C_7H_8)), reacted at room temperature in acetone (or CH_2Cl_2 for $[PtCl_2(\eta^4\text{-}C_7H_8)]$) with equimolar amounts of phosphorus ylides $Ph_3P{=}CHCO_2R$ to give the enyl complexes $[PtCl_2\{\eta^3\text{-}C_6H_{10}CH(PPh_3)CO_2R\}]$ (R = Me (**2a**), Et (**2b**)), $[PtCl_2\{\eta^3\text{-}C_{10}H_{12}CH(PPh_3)CO_2Me\}]$ (**3**), $[PtCl_2\{\eta^3\text{-}C_8H_{12}CH(PPh_3)CO_2Me\}]$ (**4**), and $[PtCl_2\{\eta^3\text{-}C_7H_8CH(PPh_3)CO_2Me\}]$ (**5**), as shown in Scheme 1. Complexes **1**−**5** were obtained as white powders after partial evaporation of the reaction solution and addition of Et_2O. They are all stable both in the solid state and in solution.

The nucleophilic attacks of some carbon and nitrogen nucleophiles on $[PtCl_2(\eta^4\text{-diene})]$ complexes have been reported. These studies include the reactivity of the same $[PtCl_2(\eta^4\text{-diene})]$ complexes whose reactivity toward ylides we have studied here. Thus, $[PtCl_2(\eta^4\text{-dicyclopentadiene})]$ reacts with acetylacetone (Hacac) or ethyl acetatoacetate (Heacac), in the presence of Na_2CO_3,[19] or with Tl(β-diketonates)[18] to give $[PtX(\eta^3\text{-}C_{10}H_{12}X)]$ (X = acac, eacac, β-diketonates) or with diethyl malonate (Hdem) to give $[PtCl(\eta^3\text{-}C_{10}H_{12}X)]_2$ (X = dem).[19] Similarly, it reacts with methanol to give $[Pt(\mu\text{-}Cl)(\eta^3\text{-}C_{10}H_{12}OMe)]$.[14,16] Those complexes, studied by NMR spectroscopy, were assigned a structure similar to that shown for **3** in Scheme 1. The corresponding

Scheme 1



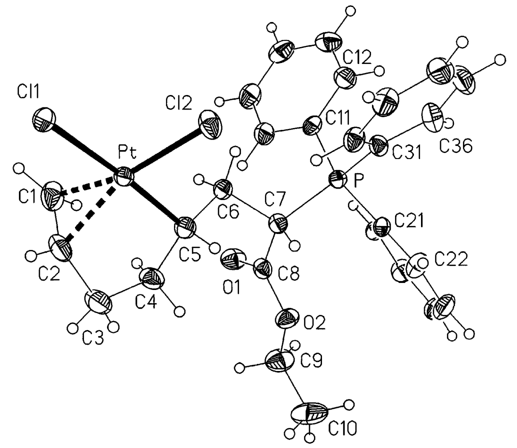


Figure 1. Ellipsoid representation of **2b** with 30% probability ellipsoids and the labeling scheme. Selected bond lengths (Å) and angles (deg): Pt−C(1) = 2.105(3), Pt−C(2) = 2.114(3), Pt−C(5) = 2.056(3), Pt−Cl(1) = 2.4286(6), Pt−Cl(2) = 2.3241(7), P−C(7) = 1.837(2), C(8)−O(1) = 1.200(3); Cl(1)−Pt−Cl(2) = 91.31(2), C(5)−Pt−Cl(2) = 89.71(8), C(1)−Pt−Cl(1) = 88.87(9), C(2)−Pt−Cl(1) = 93.56(8), C(5)−Pt−C(1) = 91.75(12), C(5)−Pt−C(2) = 83.80(11).

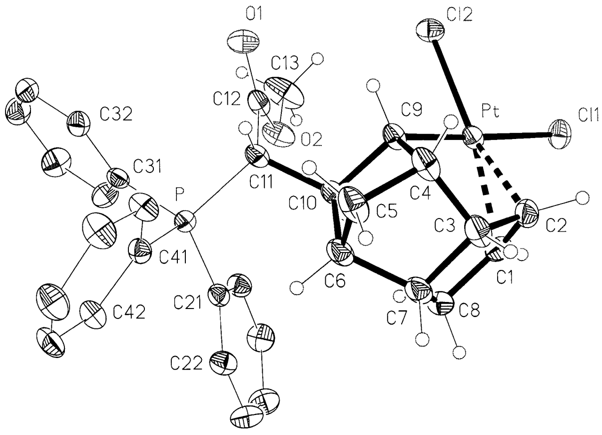


Figure 2. Ellipsoid representation of $\mathbf{3}\cdot0.5CH_2Cl_2$ (solvent omitted) with 50% probability ellipsoids and the labeling scheme. Selected bond lengths (Å) and angles (deg): Pt−C(1) = 2.163(4), Pt−C(2) = 2.119(3), Pt−C(9) = 2.040(3), Pt−Cl(1) = 2.4575(8), Pt−Cl(2) = 2.3230(8), P−C(11) = 1.843(3), C(12)−O(1) = 1.201(4); Cl(1)−Pt−Cl(2) = 90.30(3), C(1)−Pt−Cl(1) = 85.95(10), C(2)−Pt−Cl(1) = 97.84(10), C(9)−Pt−Cl(2) = 88.12(9), C(9)−Pt−C(1) = 95.85(14), C(9)−Pt−C(2) = 83.25(13).

norbornadiene complex led to metallic platinum with these nucleophiles,[19] while benzylamine ($C_7H_7NH_2$) gave the adduct $[PtCl\{\eta^3\text{-}C_{10}H_{12}(NHC_7H_7)\}]_2$, which was too insoluble to allow the determination of its molecular weight or its NMR spectrum.[19] Ammonia and primary or secondary aliphatic amines add to $[PtCl_2(\eta^4\text{-diene})]$, diene being 1,5-hexadiene or 4-vinylcyclohex-1-ene, to give $[PtCl_2\{\eta^3\text{-}C_{10}H_{12}(NRR')\}]$ or $[Pt(\mu\text{-}Cl)\{\eta^3\text{-}C_{10}H_{12}(NRR')\}]_2$.[24] However, no crystal structures of these adducts were reported. The only precedents for complexes related to **1**−**5** are those we prepared from $[PtCl_2(\eta^4\text{-cod})]$ and various carbonyl-stabilized phosphorus ylides, one of which was characterized by X-ray crystallography.[8]

X-ray Crystal Structures of 2b, $\mathbf{3\cdot0.5CH_2Cl_2}$, and $\mathbf{4\cdot2CHCl_3}$. The structures of complexes **2b** (Figure 1), $\mathbf{3}\cdot0.5CH_2Cl_2$ (Figure 2), and $\mathbf{4}\cdot2CHCl_3$ (Figure 3) show them to be monomeric. The platinum atom is in a distorted-square-planar environment, coordinated to an alkyl carbon atom, an olefinic group, and two chloro ligands in a mutually cis disposition. The greater Pt−Cl bond distance trans to the σ-C donor ligands than to the olefin (**2b**, 2.4286(6) vs 2.3241(7) Å; **3**, 2.4575(8) vs 2.3230(8) Å; **4**, 2.4307(12) vs 2.3434(12) Å) evidences the greater trans influence of σ-C donor ligands as compared to that of olefins. In addition to the previously existing chiral centers (**3**, C(3), C(4), C(6), and C(7); **4**, C(2)), the exo attack of the ylide at one of the double bonds of the diolefin ligands produces two (**2b**, C(5), C(7); **4**, C(1), C(9)) or three new chiral sites (**3**, C(9), C(10), C(11)). While in **2b** the carbon atom σ-bonded to platinum C(5) and the methyne ylide carbon atom C(7) both display the same *S* configuration, in **3** and **4** the homologous atoms are of opposite configuration (**3**, C(9) is *R* and C(11) is *S*; **4**, C(1) is *S* and C(9) is *R*). In **3**, the third chiral carbon C(10) is, like C(11), of *S* configuration. The

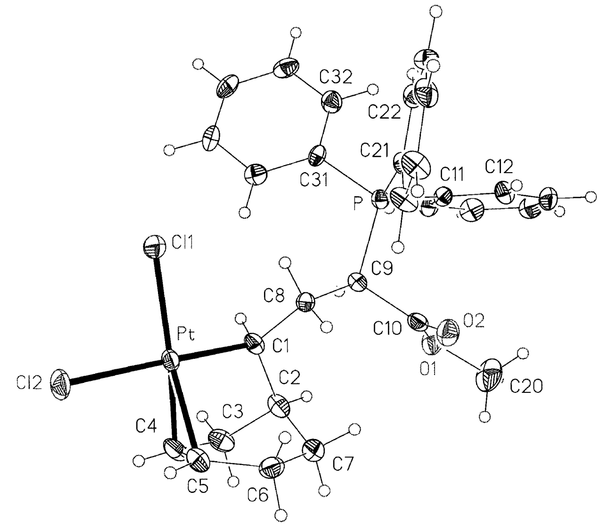


Figure 3. Ellipsoid representation of **4**·2CHCl$_3$ with 50% probability ellipsoids and the labeling scheme. Selected bond lengths (Å) and angles (deg): Pt−C(1) = 2.052(4), Pt−C(4) = 2.112(4), Pt−C(5) = 2.106(5), Pt−Cl(1) = 2.3434(12), Pt−Cl(2) = 2.4307(12), P−C(9) = 1.831(4), C(10)−O(2) = 1.193(5); Cl(1)−Pt−Cl(2) = 89.51(5), C(1)−Pt−Cl(1) = 92.31(12), C(4)−Pt−Cl(2) = 93.99(12), C(5)−Pt−Cl(2) = 89.55(12), C(4)−Pt−C(1) = 82.79(16), C(5)−Pt−C(1) = 90.36(16).

phosphorus−carbon bond lengths (**2b**, P−C(7) = 1.837(2) Å; **3**, P−C(11) = 1.843(3) Å; **4**, P−C(9) = 1.831(4) Å) are in the range found in phosphonium salts, while the C−O bond distances (**2b**, C(8)−O(1) = 1.200(3) Å; **3**, C(12)−O(1) = 1.201(4) Å; **4**, C(10)−O(2) = 1.193(5) Å) are similar to the typical values found for C(sp^2)═O in esters.[41]

The structure of **3** reveals that the attack of the ylide took place on the norbornene double bond of the fused bicyclic ring system, as was observed with other nucleophiles,[14,16,18,19] and took place, as usual, in the exo manner. The structures of **2b** and **4** show the attack at the ligands to occur at the CH$_2$ group (anti-Markovnikov). In the case of platinum complexes with monosubstituted olefins, the addition occurs with a high degree of regioselectivity according to Markovnikov's rule.[11,21−23] However, some studies on ammonia and amine additions to 1,5-hexadiene and 4-vinylcyclohexene complexes of platinum have shown the addition to be anti-Markovnikov for amines and Markovnikov for ammonia.[24] This suggests that steric rather than electronic effects are important in determining the direction of the ylide attack.

The packing diagram for **3**·0.5CH$_2$Cl$_2$ (Figure 4) shows the four shortest H bonds from CH groups (one to O(1) and three to Cl(2)), which link the molecules to layers parallel to the *xz* plane. The view direction is perpendicular to this plane. In **4**, the chloroform molecules are hydrogen bonded to both chloro ligands (H···Cl = 2.64−2.95 Å). The H···Pt distances are also relatively short (3.04, 3.18 Å), and one could thus argue that these too have hydrogen-bonding character, thus implying four-center hydrogen bonds as shown in Figure 5. However, we note that much shorter Pt···H contacts (2.48−2.75 Å) have been observed in other complexes containing a Cl$_3$C−H···Pt interaction.[42,43] In the absence of further evidence, the nature of the Pt···H contacts remains ambiguous. In the past few years an increasing number of X−H···M interactions have been reported[44−48] which, along with other weak interactions, cooperatively[49] contribute to the self-assembling of different molecules.

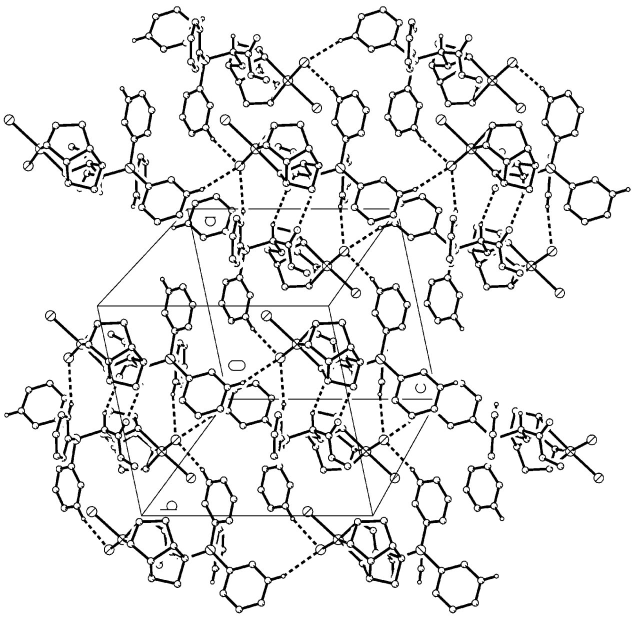


Figure 4. Packing diagram for **3**·0.5CH$_2$Cl$_2$ showing hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.

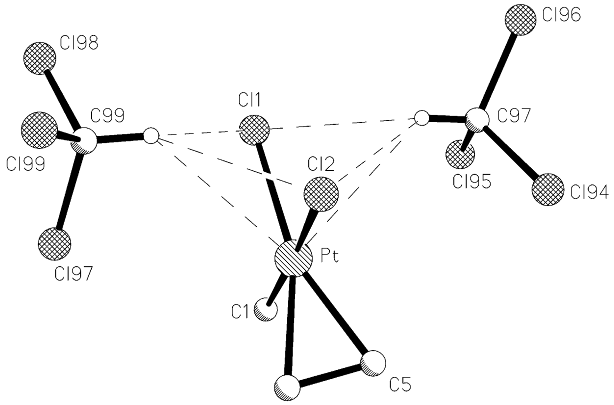


Figure 5. View of the hydrogen bond interactions in **4**·2CHCl$_3$.

NMR and IR Spectra. With the exception of **1**, all complexes have more than one chiral center. Assuming that the ylide attacks in an exo fashion, as happens in the overwhelming majority of cases and is shown here

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by the crystal structures of **2b**, **3**, and **4**, two diastereoisomers of each complex may form upon attack of the ylide, depending on the *R* or *S* configuration of the ylide carbon atom. Indeed, both the ^{1}H and the ^{31}P{^{1}H} NMR spectra of all these complexes reveal the existence of both diastereoisomers in solution, but one of them only in very small quantities. This makes it difficult to assign the ^{1}H NMR resonances. The ratio between both diastereoisomers is probably determined by steric effects. Only the resonances due to the major species are reported in the Experimental Section, but very small resonances due to the methyl protons of the CO_2R fragment of the less abundant ones are observed at 3.46 (**2a**), 1.24 (**2b**), 3.54 (**3**), 3.58 (**4**), and 3.56 ppm (**5**). Similarly, in the ^{31}P{^{1}H} NMR spectra of complexes **2**−**5** resonances due to the minor species appear at 26.08 (**2a**), 22.90 (**2b**), 26.84 (**3**), 25.22 (**4**), and 28.83 ppm (**5**).

Complexes **1**−**5** each display a multiplet due to the ylidic CH proton in the range 4.5−4.89 ppm, as expected for phosphonium salts. The CH proton in the free phosphorus ylides $Ph_3P{=}CHCO_2R$ gives rise to a broad signal at 2.82 (R = Me) or 2.85 ppm (R = Et), while the CH_2 protons of the corresponding phosphonium chlorides give doublets at 5.50 (R = Me) and 5.40 ppm (R = Et).[8] The same is observed in the ^{31}P{^{1}H} NMR spectra. The resonances of both diastereoisomers of complexes **1**−**5** (in the range 22.90−28.83 ppm) are also downfield shifted with respect to that of the corresponding ylide (R = Me, 15.3 ppm; R = Et, 17.9 ppm) or even to those observed for the phosphonium chlorides $[Ph_3PCH_2CO_2R]Cl$ (R = Me, 20.7 ppm; R = Et, 21.1 ppm).[8]

The ^{1}H NMR spectrum of complex **1** displays four singlets in the range 2.69−3.51 ppm, from the four distinct methyl groups of the tetramethylenediamine ligand, and four complex multiplets in the region 1.41−2.59 ppm, which are assigned to the protons of the alkyl group coordinated to platinum. In complexes **2**−**5**, the nonolefinic hydrogens of the enyl ligands give rise to a series of complex, often overlapping multiplets, as we observed in the spectra of the cyclooctenyl complexes obtained previously.[8]

The IR spectra of complexes **1**−**5** show a strong absorption in the 1722−1732 cm^{-1} region, assignable to $\nu_{assym}(CO_2)$, shifted to higher wavenumber with respect to that in the corresponding free ylides (R = Me, 1620 cm^{-1}; R = OEt, 1610 cm^{-1}) and close to that in the phosphonium salt (R = Me, 1720 cm^{-1}; R = OEt, 1715 cm^{-1}).

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Supporting Information Available: Listings of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **2b**, **3**·$0.5CH_2Cl_2$, and **4**·$2CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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