Platinum-Mediated P=C Bond Cleavage in a **Phosphaketene: Formation and Structure of the First** Mononuclear Diphosphaureylene Complex

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Summary: Reactions of Mes*P=C=O (1; Mes* = 2,4,6- $(t-Bu)_{3}C_{6}H_{2}$ with $(PPh_{3})_{2}Pt(C_{2}H_{4})$ (2) and $(PCy_{3})_{2}Pt$ (3; $Cy = cyclo-C_6H_{11}$ give the diphosphaureylene carbonyl complexes (L)(CO)Pt(Mes*PCOPMes*) (4, $L = PPh_3$; 5, $L = PCy_3$, respectively. The structure of 4 was determined by X-ray crystallography. Addition of dmpe $(dmpe = Me_2P(CH_2)_2PMe_2)$ to 4 or 5 gives (dmpe)Pt-(Mes*PCOPMes*) (6).

The phosphaketene $Mes*P=C=O^1$ (1; Mes* = 2,4,6- $(t-Bu)_{3}C_{6}H_{2}$) is readily decarbonylated by metal complexes to give products derived from the phosphinidene Mes*P, which may bind to the metal center² or undergo intramolecular cyclization to form the phosphaindan 2,4-(t-Bu)₂C₆H₂(6-CMe₂CH₂PH).³ We report here that the reactions of Pt(0) phosphine complexes with 1 give products containing carbonyl and diphosphaureylene [Mes*PC(O)PMes*]²⁻ ligands, derived formally from decarbonylation of the phosphaketene and coupling of the resulting phosphinidene fragment with another equivalent of the cumulene.⁴ The diphosphaureylene ligand was previously known only to bridge two metal centers.⁵

Reaction of $(PPh_3)_2Pt(C_2H_4)^6$ (2) or $(PCy_3)_2Pt^7$ (3; Cy = cyclo- C_6H_{11}) in THF with 2 equiv of 1 rapidly gives red solutions from which red crystals of the products $(R_3P)Pt(CO)[Mes^*PC(O)PMes^*]$ (4, R = Ph; 5, R = Cy) can be isolated by crystallization; the byproducts PPh₃ and PCy₃ are observed by ³¹P NMR (Scheme 1).⁸ When only 1 equiv of 1 is allowed to react with 2, the products are 4, $Pt(PPh_3)_3$, and a mixture of other unidentified Pt-P complexes.⁹ However, a 1:1 ratio of 1 and 3 gives only complex 5; free PCy₃ and unreacted starting material 3 are also observed by ³¹P NMR.

Complexes 4 and 5 were identified by IR and by multinuclear NMR spectroscopy. Complex 4 shows carbonyl bands at 2059 and 1632 cm^{-1} assigned to Pt-CO and [Mes*PC(O)PMes*] groups, respectively. Signals due to these carbons appear in the ¹³C NMR

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spectrum at δ 178.0 (ddd, ${}^{1}J_{Pt-C} = 1402 \text{ Hz}$, ${}^{2}J_{P-C} = 86 \text{ Hz}$, ${}^{2}J_{P-C} = 12 \text{ Hz}$, ${}^{2}J_{P-C} = 4 \text{ Hz}$) and δ 230.7 (ddd, ${}^{1}J_{P-C}$

(8) Synthesis of (PPh₃)(CO)Pt(Mes*PCOPMes*) (4). To a solution of $(PPh_3)_2Pt(C_2H_4)$ (2; 115 mg, 0.15 mmol) in THF (1 mL) was added Mes*PCO (1; 94 mg, 0.31 mmol) dissolved in THF (2 mL). The mixture became dark red immediately and was stirred at room temperature in the dark for a few hours. The solvent was removed under vacuum. The residue was washed with petroleum ether (bp 38-53 °C, 5 mL) to remove PPh3. The red-orange residue was dissolved in a minimal amount of THF (ca. 1 mL). A layer of petroleum ether was a minimal amount of THF (ca. 1 mL). A layer of petroleum ether was added on top of the solution. Cooling of this mixture to -25 °C gave 4 as red crystals (127 mg, 77% yield). ¹H NMR (C₆D₆): δ 7.59 (d, $4J_{P-H}$ = 2 Hz, 2H), 7.55 (d, $4J_{P-H}$ = 2 Hz, 2H), 7.30–7.23 (m, 5H), 6.91–6.78 (m, 10H), 2.06 (18H), 1.73 (18H), 1.35 (9H), 1.21 (9H). ¹³C[¹H] NMR (C₆D₆): δ 230.7 (ddd, $^{1}J_{P-C}$ = 126 Hz, $^{1}J_{P-C}$ = 92 Hz, $^{3}J_{P-C}$ = 17 Hz, quat, PCOP), 178.0 (ddd, $^{1}J_{P-C}$ = 1402 Hz, $^{2}J_{P-C}$ = 86 Hz, $^{2}J_{P-C}$ = 12 Hz, $^{2}J_{P-C}$ = 4 Hz, quat, CO), 159.7 (d, $^{2}J_{P-C}$ = 8 Hz, quat Ar), 158.4 (d, $^{2}J_{P-C}$ = 99 Hz, Ar), 134.2 (d, J_{P-C} = 12 Hz, Ar), 132.6 (d, $^{1}J_{P-C}$ = 48 Hz, ouat Ar), 131.2 (Ar), 130.3 (broad d. $^{1}J_{P-C}$ = 43 Hz, quat Ar). (dm, ${}^{1}J_{P-C} = 99$ Hz, År), 134.2 (d, $J_{P-C} = 12$ Hz, År), 1 $\overline{3}2.6$ (d, ${}^{1}J_{P-C} = 48$ Hz, quat Ar), 131.2 (Ar), 130.3 (broad d, ${}^{1}J_{P-C} = 43$ Hz, quat Ar), 129.1 (d, $J_{P-C} = 10$ Hz, Ar), 123.7 (d, ${}^{3}J_{P-C} = 7$ Hz, Ar), 122.5 (d, ${}^{3}J_{P-C} = 5$ Hz, Ar), 39.9 (d, ${}^{3}J_{P-C} = 3$ Hz, quat), 35.7 (quat), 35.3 (quat, overlaps with the next peak), 35.3 (broad, CH₃), 31.9 (CH₃); 31.8 (CH₃). ${}^{31}P_{1}H$ } NMR (CD₂Cl₂): δ 58.7 (dd, ${}^{1}J_{P+P} = 681$ Hz, ${}^{2}J_{P-P} = 177$ Hz, ${}^{2}J_{P-P} = 124$ Hz, P trans to PPh₃), 30.0 (dd, ${}^{1}J_{P+P} = 1830$ Hz, ${}^{2}J_{P-P} = 177$ Hz, ${}^{2}J_{P-P} = 15$ Hz, P trans to CO, 23.1 (dd, ${}^{1}J_{P+P} = 2246$ Hz, ${}^{2}J_{P-P} = 124$ Hz, ${}^{2}J_{P-P} = 15$ Hz, P trans to CO, 23.1 (dd, ${}^{1}J_{P+P} = 2246$ Hz, ${}^{2}J_{P-P} = 124$ Hz, ${}^{2}J_{P-P} = 15$ Hz, P trans to CO, 23.1 (dd, ${}^{1}J_{P+P} = 2246$ Hz, ${}^{2}J_{P-P} = 124$ Hz, ${}^{2}J_{P-P} = 15$ Hz, P trans to CO, 23.1 (dd, ${}^{1}J_{P+P} = 2246$ Hz, ${}^{2}J_{P-P} = 15$ Hz, P trans to CO, 23.1 (dd, ${}^{1}J_{P+P} = 2246$ Hz, ${}^{2}J_{P-P} = 15$ Hz, P trans to CO, 23.1 (dd, ${}^{1}J_{P+P} = 2246$ Hz, ${}^{2}J_{P-P} = 15$ Hz, P trans to CO, 23.1 (dd, ${}^{1}J_{P+P} = 2246$ Hz, ${}^{2}J_{P-P} = 15$ Hz, P trans to CO, 23.1 (dd, ${}^{1}J_{P+P} = 2246$ Hz, ${}^{2}J_{P-P} = 15$ Hz, P trans to CO, 23.1 (dd, ${}^{1}J_{P+P} = 15$, 2059, 1632, 1592 (shoulder), 1529, 1478, 1434, 1390, 1359, 1228, 1210, 1182, 1120, 1097, 1027, 998, 921, 902, 879, 749, 740, 708, 692, 649, 590, 527, 511 cm⁻¹. Anal. Calcd for C_{56}H_{73}O_2P_3Pt: C, 63.08; H, 6.91. Found: C, 63.05; H, 7.13. Synthesis of (**PCv**)(CO)Pt(Mes*PCOPMes*) (5). To a solution of (PCv₃)/P of (PCy₃)(CO)Pt(Mes*PCOPMes*) (5). To a solution of (PCy₃)₂Pt (3; 51 mg, 0.067 mmol) in THF (1 mL) was added Mes*PCO (41 mg, 0.135 mmol) dissolved in THF (1 mL). The mixture became dark red immediately and was stirred at room temperature in the dark for a few hours. CuCl (33 mg, 0.034 mmol) was added to complex free PCy₃ The model is the reaction. After 5 min of stirring, the solution was filtered, and the solvent was removed from the filtrate under vacuum. Complex **5** was recrystallized from petroleum ether at -25 °C (red needles) and was isolated in 45% yield (33 mg). ¹H NMR (C₆D₆): δ 7.67 (d, ⁴J_{P-H} = 2 Hz, 2H), 7.65 (broad, 2H), 2.05 (18H), 2.01 (18H), 1.96-1.24 (m, 33H), 1.35 (9H), 1.34 (9H). ¹³C{¹H} NMR (C₆D₆): δ 232.9–230.4 (m, PCOP), 180.0 (ddd, ²J_{P-C} = 78 Hz, ²J_{P-C} = 12 Hz, ²J_{P-C} = 3 Hz, Pt satellites were not observed, quat, CO), 159.7 (d, ²J_{P-C} = 10 Hz, quat Ar), 158.4 (d, ²J_{P-C} = 98 Hz, quat Ar), 151.1 (quat Ar), 150.6 (quat Ar), 138.3 (dm, ¹J_{P-C} = 98 Hz, quat Ar), 121.3 (dm, ¹J_{P-C} = 71 Hz, quat Ar), 123.9 (d, ³J_{P-C} = 7 Hz, Ar), 122.5 (d, ³J_{P-C} = 5 Hz, Ar), 40.5 (d, ³J_{P-C} = 3 Hz, quat), 39.6 (d, ³J_{P-C} = 2 Hz, quat), 37.2 (d, ¹J_{P-C} = 23 Hz, CH), 35.6 (broad, overlapping quat and CH₃), 35.3 (broad, overlapping quat and CH₃), 35.3 (broad, overlapping quat and CH₃), 35.4 (Cd₂), 27.8 (d, ³J_{P-C} = 739 Hz, ²J_{P-P} = 168 Hz, ²J_{P-P} = 136 Hz, P trans to PCy₃), 37.1 (dd, ¹J_{P+P} = 2225 Hz, ²J_{P-P} = 168 Hz, ²J_{P-P} = 15 Hz, PCy₃), 23.2 (dd, ¹J_{P+P} = 1603 Hz, ²J_{P-P} = 168 Hz, ²J_{P-P} = 15 Hz, PCy₃), 23.2 (dd, ¹J_{P+P} = 2930, 2854 (shoulder), 2037, 1637, 1593 (shoulder), 1479, 1446, 1392, 1359, 1235, 1212, 1175, 1119, 1005, 874, 738, 591 cm⁻¹, Anal. Calcd formed in the reaction. After 5 min of stirring, the solution was filtered,

2359, 2255, 1212, 1175, 1119, 1007, 1350 (shother), 1475, 1476, 1326, 1359, 1235, 1212, 1175, 1119, 1005, 874, 738, 591 cm⁻¹. Anal. Calcd for $C_{56}H_{91}O_2P_3Pt$: C, 62.02; H, 8.48. Found: C, 62.05; H, 8.77. (9) **Reaction of** (**PPh**₉)₂**Pt**(**C**₂**H**₄) (**2**; 200 mg, 0.27 mmol) in THF (1 mL) was added Mes*PCO (81 mg, 0.27 mmol) dissolved in THF (1 mL) was added Mes*PCO (81 mg, 0.27 mmol) dissolved in THF (1 mL) was added Mes*PCO (81 mg, 0.27 mmol) dissolved in the part of the mixture became dark become impediately and was THF (2 mL). The mixture became dark brown immediately and was stirred at room temperature in the dark overnight. The solvent was removed under vacuum. The brown residue was washed with petroleum ether (10 mL). Cooling the resulting petroleum ether solution to $-25~^{\rm C}$ gave 4 as a red-orange solid (75 mg, 26% yield). The remaining solid, sparingly soluble in petroleum ether, was dissolved in a minimal amount of THF (ca. 3 mL), and petroleum ether was added on top of the solution. Cooling of this mixture to -25 °C gave yellow crystals of Pt(PPh₃)₃ (64 mg, 32% yield), which was characterized by ³¹P and ¹H NMR in C_6D_6 in comparison to the literature values (Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. J. Am. Chem. Soc. **1972**, 94, 2699-2676).

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Figure 1. ORTEP diagram of 4. Selected bond lengths (Å): Pt-P1, 2.321(7); Pt-P2, 2.337(7); Pt-P3, 2.350(7); Pt-C2, 1.887(27); P1-C1, 1.865(28); P2-C1, 1.849(27). Selected bond angles (deg): P1-Pt-P2, 73.3(2); P1-Pt-P3, 105.5(2); P2-Pt-P3, 170.4(3); P1-Pt-C2, 156.3(8); P2-Pt-C2, 89.5(8); P3-Pt-C2, 94.0(8); Pt-P1-C1, 94.8(9); Pt-P2-C1, 94.7(9); Pt-P1-C16, 132.7(9); C1-P1-C16, 115.2(12); Pt-P2-C26, 112.5(8); C1-P2-C26, 126.5(12); P1-C1-P2, 97.0(13); P1-C1-O1, 128.8 (20); P2-C1-O1, 134.2(20).



= 126 Hz, ${}^{1}J_{P-C}$ = 92 Hz, ${}^{3}J_{P-C}$ = 17 Hz). The ${}^{31}P{}^{1}H{}$ NMR spectrum shows peaks due to three different phosphorus nuclei. The phosphaureylene ${}^{31}P$ nuclei show small one-bond ${}^{195}Pt-{}^{31}P$ coupling constants characteristic of terminal phosphido (PR₂) ligands.¹⁰ The different magnitudes of these couplings (681 Hz for the P trans to PPh₃ and 1830 Hz for the P trans to CO) reflect the trans influence.¹¹ The phosphaureylene P nuclei show a large cis coupling (177 Hz) and the expected large trans (124 Hz) and small cis (15 Hz) couplings to PPh₃. Spectroscopic data for **5** are similar.

The structure of 4 was confirmed by X-ray crystallography (Figure 1).¹² The coordination at Pt is distorted square planar, and the bite angle of the diphosphaureylene ligand $(73.3(2)^\circ)$ is significantly less than the idealized 90° angle. The platinum and the three coordinated P atoms lie on a plane (mean deviation 0.07 Å) with the metal carbonyl carbon 0.73 Å out of the plane. The chelating Pt-P distances (2.321(7) and 2.337(7) Å) are not significantly different, despite the different ¹J_{Pt-P} couplings observed in the ³¹P NMR spectra. Coordination at these P atoms is pyramidal, indicating that Pt-P multiple bonding is not important. The diphosphaureylene ligand is planar (mean deviation



0.03 Å), and the P–C bond lengths (1.865(28) and 1.849-(27) Å) and P–C–P bond angle $(97.0(13)^{\circ})$ in it are quite similar to those in the related four-membered ring [Mes*PCO]₂.¹³ For comparison, in the previously reported diphosphaureylene Fe₂(CO)₆ complexes, which contain five-membered MPC(O)PM' rings,¹⁴ the P–C–P angle ranges from 84.4(4) to 88.3(2)^{\circ}.

Related organic heterocycles containing diphosphaurea groups lose CO on photolysis,¹⁵ but complex 4 survived irradiation (Hg lamp, THF) for 3.5 h. It decomposes on heating in THF to 50 °C for 12 h. Reaction of 4 or 5 with dmpe (dmpe = $Me_2P(CH_2)_2PMe_2$) in THF causes displacement of a tertiary phosphine and the carbonyl ligand to yield the orange, sparingly soluble (dmpe)Pt(Mes*PCOPMes*) (6) (Scheme 2).¹⁶ This reaction proceeds quickly at ambient temperature for 4 but requires heating to 60 °C for 2 days for 5. As expected, the IR spectrum of 6 shows only one CO stretch (1601 cm^{-1}), and the ³¹P NMR spectrum is an AA'BB' pattern. The diphosphaureylene P nuclei have a large cis coupling of 158 Hz, in contrast to the dmpe cis P-Pcoupling of 10 Hz, and a trans P-P coupling of 216.5 Hz. As in 4 and 5, the $^{195}Pt-^{31}PR_2$ coupling is characteristically small (1103 Hz). Complex 6 remains unchanged on heating in CH₂Cl₂ at 40 °C for 3 days and in THF at 65 °C for 4 h. It decomposes on irradiation (Hg lamp, THF) for 6 h.

The formation of ureylene derivatives from metalmediated isocyanate coupling may proceed via metalimido complexes, and this step has been directly observed.¹⁷ We are currently investigating the possibility

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⁽¹²⁾ Crystal data for 4: $C_{56}H_{73}O_2P_3Pt$, orthorhombic, $P2_12_12_1$, V = 5432(3) Å³, Mo K α ($\lambda = 0.710$ 73 Å), $d_{calc} = 1.304$ g/cm³, a = 15.944(5) Å, b = 17.037(5) Å, c = 19.998(7) Å, T = 230 K, Z = 4, R(F) = 6.86%, R(wF) = 8.05%. Details of the structure determination are provided as supporting information.

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⁽¹⁶⁾ Synthesis of (dmpe)Pt(Mes*PCOPMes*) (6). To a solution of 4 (133 mg, 0.125 mmol) in THF (1 mL) was added dmpe (18.8 mg, 0.125 mmol) dissolved in THF (2 mL). The red mixture was stirred at room temperature and became orange after a few hours. The solvent was removed under vacuum. The orange residue was washed with petroleum ether (20 mL) and then recrystallized by diffusion of petroleum ether into THF at -25 °C to give 71 mg of orange crystals (61% yield). ¹H NMR (CD₂Cl₂): δ 7.34 (broad, 4H), 1.71 (36H), 1.55–1.43 (m, 4H), 1.28 (18H), 1.01–0.89 (m, 12H). ¹³C(¹H) NMR (CD₂Cl₂): δ 237.2–233.8 (m, quat, PCOP), 158.7 (m, quat Ar), 149.5 (quat Ar), 137.2 (dm, ¹J_{P-C} = 75 Hz, quat Ar), 121.9 (Ar), 39.1 (quat), 35.0 (quat), 34.2 (CH₃), 31.6 (CH₃), 30.1–29.1 (m, CH₂), 15.6–14.6 (m, CH₃). ³¹P(¹H) NMR (CD₂Cl₂): δ 32.0 (¹J_{P+P} = 2435 Hz, dmpe), 14.0 (¹J_{P+P} = 1103 Hz, Mes*P), AA'BB' pattern, ²J_{PP(ris, AB} = -5.5 Hz. IR (KBr): 3068, 2957, 2907 (shoulder), 2861, 1601, 1477, 1434, 1417, 1389, 1358, 1296, 1286, 1237, 1211, 1123, 1026, 989, 952, 941, 899, 872, 839, 794, 73, 715, 696, 656, 589, 549, 510 cm⁻¹. Anal. Calcd for C₄₃H₇₄OP₄Pt: C, 55.76; H, 8.07. Found: C, 55.46; H, 8.19.

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that diphosphaureylene complexes 4 and 5 are formed from a related metal-phosphinidene species.

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