Synthesis and Reactivity of (dppe)Pt(OMe)$_2$ [dppe = 1,2-bis(diphenylphosphino)ethane]

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Synthesis of (dppe)Pt(OMe)$_2$ (**1**) [dppe = 1,2-bis(diphenylphosphino)ethane] by NaOMe metathesis on the analogous dichloride is reported along with the thermal and carbonylation chemistry of (**1**); the release of dimethyl carbonate and dimethyl oxalate from the carbonylation product (dppe)Pt(CO$_2$Me)$_2$ was accomplished by thermal and oxidative techniques.

Palladium-catalysed oxalate ester synthesis,[1] sometimes promoted by alkyl nitrites,[1b] has been investigated as a syn-gas-based route to ethylene glycol. Little mechanistic information is available about the transformation, but the carbonylation of metal–oxygen bonds may play a key role. We report here the synthesis of the first well characterized bis-alkoxide complex of the group 8 metals and its reaction with two equivalents of CO to generate a bis-methoxycarbonyl product.

Reaction of (dppe)PtCl$_2$ [dppe = 1,2-bis(diphenylphosphino)ethane, Ph$_2$PCH$_2$CH$_2$PPh$_2$] with excess of sodium methoxide in benzene–methanol yields the highly reactive molecule, (dppe)Pt(OMe)$_2$, (**1**), equation (1). This complex is thermally unstable† decomposing in a few hours in CD$_2$Cl$_2$ solution at 25 °C to yield methanol, formaldehyde oligomers, and traces of CO. The rate of decomposition in [^{2}H$_8$]tetrahydrofuran (THF) is much slower at room temperature but comparable at 55 °C. The rate of decomposition in α,α′-dimethyl THF is comparable to that in CD$_2$Cl$_2$ suggesting that β-elimination from a methoxide ligand requires an open co-ordination site which can be blocked by donor solvents such as THF.[2] One novel, unstable organometallic product of the decomposition has been identified by ^{1}H and ^{31}P n.m.r. spectroscopy as (dppe)Pt(CO$_2$Me)(OMe),(**2**),‡ formed from (**1**) and the small amount of CO which results from decomposition of a methoxide ligand.

Complex (**1**) reacts in either [^{2}H$_8$]THF or CD$_2$Cl$_2$ with two equivalents of CO to form a single new product, (**3**), in which the two CO molecules have been incorporated, stepwise, into the M–O bonds of (**1**). The reaction proceeds through intermediate (**2**), equation (2). Complex (**3**) was identified by ^{1}H, ^{31}P, and ^{13}C n.m.r. spectroscopy,‡ and the structure was confirmed crystallographically. The structure of (**3**) is shown in Figure 1.§

$$(\text{dppe})\text{PtCl}_2 + \text{NaOMe (excess)} \xrightarrow{\text{C}_6\text{H}_6\text{–MeOH}} \underset{(\mathbf{1})}{(\text{dppe})\text{Pt(OMe)}_2} \qquad (1)$$

$$(\mathbf{1}) + \text{CO} \longrightarrow \underset{(\mathbf{2})}{(\text{dppe})\text{Pt(CO}_2\text{Me)(OMe)}} \xrightarrow{\text{CO}} \underset{(\mathbf{3})}{(\text{dppe})\text{Pt(CO}_2\text{Me)}_2} \qquad (2)$$

Complex (**3**) is indefinitely stable at 25 °C but decomposes slowly at temperatures as low as 80 °C to generate CO, methanol, and formaldehyde oligomers. This decarbonylation can be inhibited by heating (**3**) in the presence of CO; under 3 atmospheres, decomposition requires temperatures in excess of 130 °C. Under 12 atmospheres of CO, decomposition takes place only above 160 °C and then the observed products include methanol, formaldehyde oligomers, CO$_2$, and dimethyl carbonate.¶ Oxidation of (**3**) using stoicheiometric or catalytic amounts of NOPF$_6$, AgBF$_4$, or AgPF$_6$ takes place in minutes at 25 °C, resulting in a complex mixture which includes dimethyl oxalate, dimethyl carbonate, methyl formate, CO, CO$_2$, methanol, and formaldehyde oligomers. This final result suggests a role for alkyl nitrite promoters in the reaction: all three reaction pathways observed in the thermal decomposition of (**3**), decarbonylation, reductive elimination, and β-hydride elimination, are greatly accelerated by one electron oxidation.

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† Because of this reactivity, recrystallization degrades (**1**). Washing in THF lowers the yield of (**1**), though the greater solubility of dark impurity allows purification by this method. The reactivity of this complex has made obtaining elemental analysis data impossible. N.m.r. data: ^{1}H (CD$_2$Cl$_2$–CDHCl$_2$) : δ 7.4—8.2(m, 20H), 3.6 [dd, Pt satellites, *J*(PH) 6.4, 0.7, *J*(PtH) 37.2 Hz, 20H], and 1.9—2.5 (m, 4H); ^{31}P (CD$_2$Cl$_2$) δ 25.7 p.p.m. [s, Pt satellites *J*(PtP) 3287 Hz] (relative to external 85% H$_3$PO$_4$).

‡ The intermediate (**2**) has not been isolated and the ^{1}H n.m.r. spectrum overlaps with that of the starting complex (**1**). However, a new PtOMe resonance at δ 3.80 [d, Pt satellites, *J* (PH) 6.0, *J*(PtH) 35 Hz] and a new PtCO$_2$Me resonance at δ 3.26 [s, Pt satellites, *J*(PtH) 4.5 Hz] which integrate as 1:1 are seen. Similarly, the ^{31}P n.m.r. spectrum is consistent with this assignment: (CD$_2$Cl$_2$) δ 37.8 p.p.m. [d, Pt satellites, *J*(PP) 7.6, *J*(PPt) 4119 Hz], 33.3 [d, Pt satellites, *J*(PP) 7.6, *J*(PtP) 2977 Hz in 1:1 ratio]; a weak i.r. band at 1690 cm^{-1} is also seen. *Data for* (**3**): n.m.r. ^{1}H (CD$_2$Cl$_2$/CDHCl$_2$) δ 7.2—7.9 (complex m, 20H), 3.21 [s, Pt satellites, *J*(PtH) 4.9 Hz, 6H], and 2.2—2.4 (complex m, 4H); ^{31}P (CD$_2$Cl$_2$) δ 39.45 p.p.m. [s, Pt satellites, *J*(PtP) 1849 Hz]; ^{13}C (CD$_2$Cl$_2$) δ 193.97 [dd, Pt satellites, *J*(PC) 11.2, 147.9, *J*(PtH) 1250 Hz], 130.68 [d, Pt satellites, *J*(PC) 49.6, *J*(PtC) 27.4 Hz], 133.64 [3 lines, Pt satellites, *J*(PC) 11.9, *J*(PtC) 27.4 Hz], 129.23 [3 lines, *J*(PC) 10.9 Hz], 131.59 (s), 49.32 [s, Pt satellites, *J*(PtC) 29.5 Hz], and 28.39 [dd, Pt satellites, *J*(PC) 12.8, 35.2, *J*(PtC) 24.7 Hz]; i.r. (CH$_2$Cl$_2$) 1650(s) and 1680(sh) cm^{-1}.

§ *Crystal data for* (**3**): C$_{30}$H$_{30}$O$_4$P$_2$Pt, *M* = 606.70, triclinic, space group C_i^1-$P\bar{1}$ (No. 2), *a* = 11.075(3), *b* = 14.565(4), *c* = 9.105(2) Å, α = 96.30(2), β = 100.45(2), γ = 76.49(2)°, *U* = 1401(1) Å^3, *Z* = 2, D_c = 2.149 g cm^{-3}. Intensity data were collected using a Syntex P3 diffractometer, Mo-K_α (λ = 0.71069 Å) radiation, graphite monochromator, −100 °C, Ω scans of 1.3°; $4 < 2\theta < 55°$. 6670 Unique reflections were collected, an absorption correction was applied; μ = 102.26 cm^{-1} (PDP-11 computer using local modification of SDP-plus software supplied by Enraf–Nonius Corp.); transmission factors: 59.25—99.67. The structure was solved by Patterson synthesis and refined by a combination of least squares and Fourier syntheses. The H atoms were found and included in idealized positions [*d*(C–H) 0.95 Å, B_H = 4.0] as a fixed contribution. A full matrix [least-squares refinement, 37 anisotropic atoms, 334 variables] of 5837 observations with [$F_o^2 > 3\sigma F_o^2$)], gave *R* = 0.027, R_w = 0.033. The final Fourier residuals gave ≤ 1.80 e Å^{-3} surrounding Pt atom. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¶ Control experiments show that dimethyl oxalate is decomposed under these reaction conditions (apparently by an unidentified platinum species). All organic products were identified by g.c.–mass spectrometry. Up to 40% yields of dimethyl carbonate were realized in these thermolyses under CO.

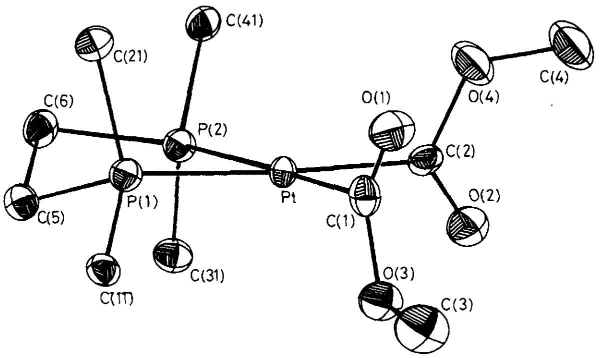

Figure 1. Perspective drawing of the co-ordination sphere of (**3**). Only the *ipso*-phenyl carbon atoms are included and the H atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

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2 Formally this reaction is similar to that studied by Whitesides and coworkers involving thermal decomposition of Pt^{II} diethyl complexes. See for example: R. G. Nuzzo, T. J. McCarthy, and G. M. Whitesides, *Inorg. Chem.*, 1981, **20**, 1312; G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Am. Chem. Soc.*, 1972, **94**, 5258; G. M. Whitesides, *Pure Appl. Chem.*, 1981, **53**, 287; J. McDermott, J. F. White, and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521; T. J. McCarthy, R. G. Nuzzo, and G. M. Whitesides, *ibid.*, 1981, **103**, 3396; P. Foley, R. DiCosimo, and G. M. Whitesides, *ibid.*, 1980, **102**, 6713; R. DiCosimo, S. S. Moore, A. R. Sowinski, and G. M. Whitesides, *ibid.*, 1981, **104**, 124; R. G. Nuzzo, T. J. McCarthy, and G. M. Whitesides, *ibid.*, 1981, **103**, 3404; R. DiCosimo and G. M. Whitesides, *ibid.*, 1982, **104**, 3601; S. S. Moore, R. DiCosimo, A. F. Sowinski, and G. M. Whitesides, *ibid.*, 1981, **103**, 948.