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Evidence for Platinum(II) Oxo Intermediates in Reactions of (Diphosphine)platinum(II) Carbonate Complexes

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Introduction

Low-valent, late-metal oxo complexes are of much current interest and speculation.[1−5] In the course of our studies of (diphosphine)platinum(II) alkoxide and carbonate complexes, (LL)Pt(OR)$_2$[6] and (LL)Pt(CO$_3$),[7] we encountered interesting reactions of these complexes with L′ (L′ = PR$_3$, CO, etc.) that yield Pt(0) complexes and oxidized L′. Further investigations of some of these reactions, reported here, implicate the intermediacy of (LL)(L′)Pt$^+$−O$^-$ species.

Experimental Section

General Procedures. Reactions were conducted under argon using glovebox, vacuum line, and Schlenk techniques. Dichloromethane-*d*$_2$ was vacuum-transferred from calcium hydride. The complexes (dppe)Pt(CO$_3$) and (dppp)Pt(CO$_3$) were prepared as described in the literature[7−9] [dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dcpe = 1,2-bis(dicyclohexylphosphino)ethane].

Reaction of (dppe)Pt(CO$_3$) with Carbon Monoxide. CD$_2$Cl$_2$ (0.5 mL) was vacuum-transferred onto solid (dppe)Pt(CO$_3$) (8 mg, 12.2 μmol) in a 5 mm NMR tube equipped with a J. Young valve. The resulting suspension was treated with CO gas (1 atm) and allowed to reach saturation. No color change was evident after 1 h at ambient temperature. The tube was heated under reflux for approximately 1 h, whereupon the mixture turned light orange. Analysis of the mixture by ^{31}P NMR spectroscopy showed the formation of a small amount of (dppe)Pt(CO)$_2$ (δ 24.3 (s, J_{PtP} = 3095 Hz)).[10] The reaction mixture was allowed to stand at ambient temperature for 23 d, by which time it had turned dark orange. Analysis of the homogeneous solution by ^{31}P NMR spectroscopy indicated that all of the (dppe)Pt(CO$_3$) had been consumed to give (dppe)Pt(CO)$_2$ (92%) and (dppe)PtCl$_2$ (8%). A ^{13}C NMR spectrum showed a small singlet at δ 125.3 assigned to CO$_2$ on the basis of a comparison with the spectrum of an authentic sample.

Isotope Exchange Reactions of (dppp)Pt(^{13}CO$_3$). A. With ^{12}CO$_2$ Alone. A 5 mm NMR tube equipped with a J. Young valve was loaded under argon with (dppp)Pt(^{13}CO$_3$) (3.0 mg, 4.5 μmol) (prepared from (dppp)PtCl$_2$ and Ag$_2$^{13}CO$_3$)[8] dissolved in CD$_2$Cl$_2$ (0.61 mL). ^{1}H NMR spectroscopy confirmed that the sample was free of water, and a ^{13}C NMR spectrum showed the carbonate carbon at δ 167.6 (t, J_{PC} = 3.6 Hz) with no evidence of free ^{13}CO$_2$. The tube was opened and the solution saturated with CO$_2$ (Linde research grade) by purging for 60 s through an oven-dried 20-gauge needle. The tube was immediately recapped under carbon dioxide and shaken several times. After 17 h, a ^{13}C NMR spectrum showed that the ^{13}C-enriched carbonate peak at δ 167.6 was still present, along with a new peak at δ 125.3 due to free ^{13}CO$_2$. A ^{31}P NMR spectrum indicated roughly 30% exchange on the basis of the intensity of the singlet at δ −12.05 due to (dppp)Pt(^{12}CO$_3$), observed in the center of the doublet (J_{PC} = 3.6 Hz) due to (dppp)Pt(^{13}CO$_3$). A ^{1}H NMR spectrum showed the presence of a trace of water (3% vs Pt), most likely introduced when the CO$_2$ was added. After 45 h, the exchange had progressed further but still had not gone to completion.

B. With ^{12}CO$_2$ in the Presence of H$_2$O. A similar experiment was conducted with (dppp)Pt(^{13}CO$_3$) (2.6 mg, 3.9 μmol) dissolved in CD$_2$Cl$_2$ (0.54 mL). Water (0.1 μL, 6 μmol, 1.6 equiv) was added at the time of purging with CO$_2$. The ensuing slow exchange was observed by monitoring the ^{31}P NMR spectra every 0.5 h for 5.5 h. After 3−4 h, exchange had reached ca. 30%, but even after 15 h, the exchange was not quite complete.

C. With ^{12}CO$_2$ in the Presence of dppp. A third experiment was carried out using (dppp)Pt(^{13}CO$_3$) (2.6 mg, 3.9 μmol) dissolved in CD$_2$Cl$_2$ (0.54 mL), except that solid dppp (2.0 mg, 4.8 μmol, 1.25 equiv, recrystallized from ethanol) was added before the CO$_2$ purge. The subsequent rapid isotope exchange was observed by monitoring the ^{31}P NMR spectra every 5 min. In less than 5 min, the exchange had gone to over 30% completion and was essentially complete by 40 min. This was confirmed by the complete absence of the ^{13}CO$_3$ peak of (dppp)Pt(^{13}CO$_3$) in the ^{13}C NMR spectrum at ~1 h.

Reactions of (dppp)Pt(CO$_3$) with dppp. A. Reaction of (dppp)Pt(^{13}CO$_3$). A 5 mm NMR tube equipped with a J. Young valve was loaded under argon with (dppp)Pt(^{13}CO$_3$) (2.6 mg, 3.9 μmol) and dppp (5.6 mg, 13.6 μmol, 3.5 equiv, recrystallized) dissolved in CD$_2$Cl$_2$ (0.54 mL). After 19 h, the solution had turned yellow and a ^{31}P NMR spectrum showed ~4.5% conversion to Pt(dppp)$_2$ (δ −10.4, J_{PtP} = 3646 Hz, identified by spectral comparison with an authentic sample)[11] and (3-(diphenylphosphino)propyl)diphenylphosphine oxide (dpppO: δ 30.8 (d, J_{PP} = 1.5 Hz), −17.7 (d, J_{PP} = 1.5 Hz)).[12,13]

B. Reaction in the Presence of Water. After 24 h, water (0.15 μL, 8.3 μmol, 2.1 equiv) was added to the above NMR tube, and the reaction was further monitored by ^{31}P NMR. The reaction still proceeded relatively slowly, increasing from 6% conversion prior to the addition of water to 11% at 1 h after addition and 25% at 9 h.

C. Reactions at Higher Concentrations. A more concentrated reaction was run using (dppp)Pt(^{13}CO$_3$) (5.2 mg, 7.8 μmol) and dppp (11.2 mg, 27.2 μmol, 3.5 equiv, recrystallized) in CD$_2$Cl$_2$ (0.50 mL). Even after vigorous shaking for several minutes, small amounts of solids remained undissolved. The reaction was monitored by ^{31}P NMR, showing a conversion of 11% at 12 h, 18% at 3 d, and ~25% at 13 d. An almost identical reaction using (dppp)Pt(CO$_3$) prepared from (dppp)PtCl$_2$ and sodium isopropoxide gave very similar results, as did a reaction with a fresh lot of dppp used as received from Strem and a reaction that included 0.3 equiv of OPPh$_3$.

D. Reaction with "Active" dppp. A similar reaction was run using (dppp)Pt(CO$_3$) (5.7 mg, 8.5 μmol) (shown to be water-free by ^{1}H NMR) and an older, unrecrystallized sample of dppp from Strem (12.1 mg, 29.3 μmol, 3.4 equiv) in CD$_2$Cl$_2$ (0.5 mL). The reaction mixture immediately turned yellow, and ^{31}P NMR analysis showed 8% conversion at 8 min, 11% conversion at 24 min, and 68% conversion at 23 h on the basis of Pt(dppp)$_2$ formed. The last spectrum also showed the formation of ca. 0.6 equiv of dpppO per Pt(dppp)$_2$. The only impurities in the "active" dppp used in this experiment that could be detected by ^{1}H and ^{31}P NMR were dpppO$_2$ (4%), dpppO (0.8%), and OPPh$_3$ (0.3%). The same rapid reaction rate was observed in a number of different experiments with this particular lot of dppp.

E. Reaction in the Presence of Carbon Dioxide. A solution of (dppp)Pt(CO$_3$) (64.5 mg, 97 μmol) in CH$_2$Cl$_2$ (10 mL, dried over

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molecular sieves) under argon was bubbled with carbon dioxide, and then a solution of dppp (61 mg, 148 μmol, 1.53 equiv, “active” Strem lot) in dry CH_2Cl_2 (3 mL) was added dropwise. A small amount of white precipitate formed. After 6 d, the reaction mixture still had not turned the yellow color characteristic of $Pt(dppp)_2$ and a ^{31}P NMR spectrum showed mostly unreacted $(dppp)Pt(CO_3)$ and dppp, no $Pt(dppp)_2$, and only small amounts of dpppO and $dpppO_2$. Similarly, no $Pt(dppp)_2$ was detected in the carbon dioxide isotope exchange reactions described above utilizing recrystallized dppp.

F. Reaction in the Presence of Water and Carbon Dioxide. A solution of $(dppp)Pt(CO_3)$ (41.7 mg, 63 μmol) in dry CH_2Cl_2 (8 mL) under argon was treated with a solution of dppp (36 mg, 86 μmol, 1.38 equiv, new Strem lot) in dry CH_2Cl_2 (2 mL). Water (10 μL, 550 μmol, 9 equiv) was then added. After for 1 h of stirring, the solution had turned slightly yellow but no precipitate had formed. The solution was then bubbled with carbon dioxide, resulting in the immediate formation of a white precipitate. The precipitate was isolated by centrifugation, washed with CH_2Cl_2 (5 mL), and dried under vacuum to give $[Pt(dppp)_2{}^{2+}][HCO_3{}^-]_2$ (62 mg, 86%), identified by ^{31}P NMR (δ −5.5 (J_{PtP} = 2188 Hz) in CD_3OD; cf. δ −5.8 (J_{PtP} = 2190 Hz) for $[Pt(dppp)_2{}^{2+}][Cl^-]_2$ prepared according to the literature).[14]

Reaction of $(dppp)Pt(CO_3)$ with CS_2. Carbon disulfide (5 μL, 83 μmol, 33 equiv) was added to a solution of $(dppp)Pt(CO_3)$ (1.7 mg, 2.5 μmol) in CH_2Cl_2/CD_2Cl_2 (~0.5 mL). After 2 d, *ca.* 4% $(dppp)Pt(S_2CO)$ (δ −4.9, J_{PtP} = 2900 Hz, identified by spectral comparison with an authentic sample (vide infra)) had formed. An aliquot of dppp (0.5 mg, 1.2 μmol, 0.5 equiv, “active” Strem lot) was then added. After 4 h, a ^{31}P NMR spectrum showed that the reaction had proceeded to 17% conversion, increasing to 69% conversion at 23 h. In a similar reaction starting with 3.3 mg of carbonate complex and 100 μL of CS_2 and ca. 0.2 equiv of dppp, no carbonate remained after 4 d. In addition to the dithiocarbonate complex, ca. 5% of another complex was detected by ^{31}P NMR (δ −3.6 (J_{PtP} = 2885 Hz)), tentatively assigned to $(dppp)Pt(S_2CS)$.

Synthesis of Authentic $(dppp)Pt(S_2CO)$.[15] A solution of dppp (240 mg, 582 μmol, 1.09 equiv) in chloroform (3 mL) was added to a solution of $Pt(S_2COEt)_2$[16] (234 mg, 535 μmol) in chloroform (4 mL). The resulting yellow solution started to deposit a white precipitate within a few minutes. After 1.25 h, the product was isolated by filtration, washed with ether, and dried under vacuum to give essentially pure $(dppp)Pt(S_2CO)$ (228 mg, 61%). An analytical sample was prepared by diffusing hexane into a dichloromethane solution of the complex. ^1H NMR (CD_2Cl_2): δ 2.12 (m, 2 H), 2.69 (m, 4 H), ~7.4 (m, 12 H), ~7.6 (m, 8 H). ^{31}P NMR (CD_2Cl_2): δ −4.9 (J_{PtP} = 2900 Hz). Anal. Calcd (found) for $C_{28}H_{26}OP_2PtS_2$: C, 48.06 (48.19); H, 3.75 (3.58).

Results

In the course of our studies of $L_2Pt^{II}Y_2$ complexes (Y = $OSiMe_3$, OR, OH; Y_2 = CO_3),[6,7] we repeatedly encountered reactions of these complexes, particularly in the presence of added L′ (L′ = PR_3, CO, CNR, $OSiMe_3{}^-$), that led to the formation of $Pt^0L_nL'_{4-n}$ and L′O. Several examples, described in detail in the Experimental Section and Supporting Information, are summarized in eqs 1−3.

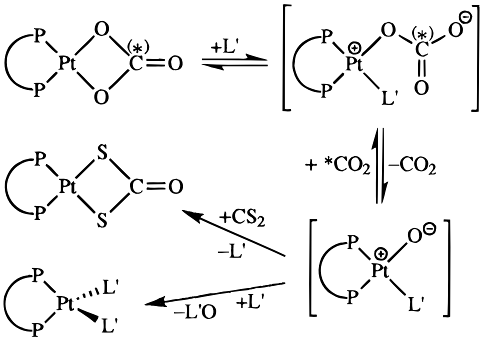
$$(dppe)Pt(CO_3) + 3CO \rightarrow (dppe)Pt(CO)_2 + 2CO_2 \quad (1)$$

$$(dppe)Pt(OSiMe_3)_2 + PMe_3 \rightarrow (dppe)Pt(PMe_3)_2 + OPMe_3 + (Me_3Si)_2O + ... \quad (2)$$

$$(dppe)Pt(CO_3) + t\text{-BuNC} \rightarrow [??] \rightarrow (dppe)_2Pt + t\text{-BuNCO} + ... \quad (3)$$

It appeared that these reactions might be proceeding via $L_2L'Pt^+{-}O^-$ species. A considerable amount of effort was therefore exerted to find an L/Y/L′ system for which the chemistry was clean enough to permit the kind of detailed studies that would be needed to thoroughly explore this hypothesis. In many cases, unfortunately, ^{31}P NMR spectra of the reaction mixtures showed perplexing sets of signals in addition to those from the “expected” products. For example, in the reaction of $(dppe)Pt(OSiMe_3)_2$ or $(dppe)Pt(CO_3)$ with dppe, were observed not only $Pt(dppe)_2$ and dppe oxides but also a large number of signals that could not be assigned due to the complexity of the resulting product mixtures. Furthermore, some of these signals exhibited unusual chemical shifts and $^{195}Pt{-}^{31}P$ coupling constants (see Supporting Information). Qualitatively, we observe that the rates of formation of Pt(0) products in these reactions follow the orders Y = OH ≫ OR, L_2 = dppp > dppe > dcpe, and L′ = dppp ≫ PPh_3.

Scheme 1. Reactions of $(dppp)Pt(CO_3)$ and Proposed Intermediates



The most convincing evidence that we have found for an $L_2L'Pt^+{-}O^-$ species is provided by the reactions of $(dppp)Pt(CO_3)$ shown in Scheme 1. Treatment of $(dppp)Pt(^{13}CO_3)$ with $^{12}CO_2$ leads to the slow formation of $(dppp)Pt(^{12}CO_3)$ and $^{13}CO_2$. This isotope exchange reaction occurs about 4−5 times faster in the presence of 1−2 equiv of water but 200 times faster in the presence of 1.25 equiv of added dppp. No other reaction besides isotope exchange is observed under any of these conditions. In the *absence* of added CO_2, however, the addition of dppp to $(dppp)Pt(CO_3)$ leads to a net redox reaction and the slow formation of $Pt^0(dppp)_2$ and dpppO. This reaction is strongly inhibited by CO_2, as indicated by both the exchange studies and separate test reactions. (When both water and carbon dioxide are present, the reaction of $(dppp)Pt(CO_3)$ with dppp leads instead to the very rapid precipitation of $[Pt(dppp)_2]^{2+}$, presumably as the bis(bicarbonate) salt.) In a reaction closely related to carbon dioxide isotope exchange, $(dppp)Pt(CO_3)$ reacts with CS_2 to give $(dppp)Pt(S_2C{=}O)$ (presumably via isomerization of an intermediate $(dppp)Pt(OSC{=}S)$ complex), again requiring the presence of added dppp to achieve a significant reaction rate.

We have not carried out full kinetic studies on the reaction of $(dppp)Pt(CO_3$ with dppp, but a number of reactions conducted at varying concentrations of both platinum carbonate and added phosphine gave initial rates in the absence of water and carbon dioxide that were consistent with the assumption of a second-order reaction having a rate constant equal to 5×10^{-5} M^{-1} s^{-1}. Furthermore, this rate (a) is not dependent on the source of the carbonate complex (e.g., synthesis via Ag_2CO_3 or NaO-*i*-Pr),[8] (b) is only moderately influenced by the addition of as much as 1−2 equiv of water ($k_0 \approx 5 \times 10^{-4}$ M^{-1} s^{-1}), and (c) is not influenced at all by the addition of 0.3 equiv of either $dpppO_2$ or $OPPh_3$ or excess LiCl. One older lot of commercial “active” dppp, whose only observable impurities were phosphine oxides, gave initial rates nearly 2 orders of magnitude higher

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(ca. 3×10^{-3} M^{-1} s^{-1}). We have not been able to identify the origin of this accelerating effect.

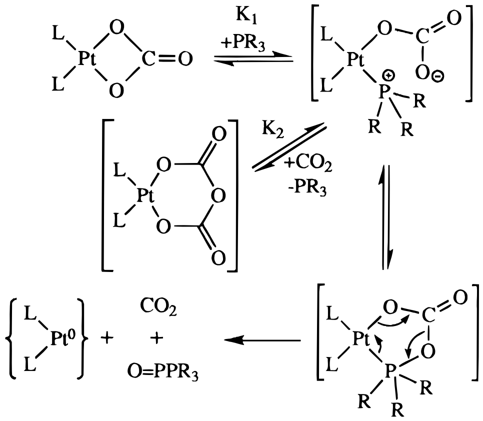
Discussion

Previous reports have described reactions of (diphosphine)-platinum(II) carbonate complexes with substrates such as carbon monoxide or phosphine that led to Pt(0) species and oxidized substrate.[17−20] The exact nature of these reactions has not been clearly identified and is complicated by the fact that many of these reactions were run in alcoholic solvents where alcohol/carbonate equilibria may be occurring,[7] leading to reduction by β-hydrogen elimination from coordinated alkoxide.[21] The present studies offer a more detailed picture of the reduction of platinum carbonates in nonhydroxylic solvents.

Addition of phosphine (L′) to L_2PtCl_2 is well-known to lead to the formation of $[L_2L'PtCl]^+$;[22,23] thus reaction of $L_2Pt(CO_3)$ with L′ might be expected to lead to carbonate chelate ring opening and formation of the monodentate carbonate complex $[L_2L'Pt^+OCO_2^-]$ shown in Scheme 1. This reaction must have a low equilibrium constant, as such species are not directly observed. Subsequent reversible dissociation of carbon dioxide from the monodentate carbonate would generate the proposed $L_2L'Pt^+{-}O^-$ intermediate. This complex would then readily react with either CS_2 or $^*CO_2$ to re-form, on dissociation of L′, $L_2Pt(Y_2CO)$, Y = O or S, as is experimentally observed. Alternatively, deoxygenation of the oxo intermediate by L′ would lead to formation of L′O, e.g., phosphine oxide, and $Pt^0L_nL'_{4-n}$, again as observed. Most convincing is the observed strong inhibition of this latter reaction by added carbon dioxide.

A plausible alternative explanation for the observed reactions would be catalysis by water, via such species as $L_2Pt(OH)(OCO_2H)$. We rule out this pathway as a *primary* contributor since the intentional addition of water in amounts of 1−2 equiv, a hundred times that adventitiously present (less than 0.01−0.02 equiv), has only a 4−10-fold effect on the observed reaction rates. The strong accelerating effect of added phosphine on CS_2 and $^*CO_2$ exchange is also not as readily accommodated by such an alternative explanation. Acceleration by acid, e.g., in the "active" dppp, is deemed unlikely, as addition of CH_3CO_2H to (dppp)$Pt(CO_3)$ leads to formation of (dppp)Pt(OAc) and H_2CO_3, which in the presence of (dppp)$Pt(CO_3)$ and dppp leads to rapid precipitation of $[Pt(dppp)_2]^{2+}$ (vide supra).

Scheme 2. Alternate Mechanism for Reduction of $L_2Pt(CO_3)$ by PR_3



Another possible mechanism is the formation of phosphonium intermediates[24] by interaction of the added phosphine with one of the carbonate oxygen atoms, a variation of which is illustrated in Scheme 2. Inhibition by carbon dioxide would require that either (a) the formation of phosphine oxide and carbon dioxide be measurably reversible or (b) there be a favorable equilibrium K_2 for formation of a diketotrioxametallacyclohexane−CO_2 adduct. The former seems most unlikely due to the high thermodynamic stability of the products. This argument is supported by the lack of reaction of $Pt(PPh_3)_4$ with carbon dioxide and triphenylphosphine oxide. The latter explanation, which would also accomplish isotope exchange, requires a large formation constant K_2 to explain CO_2 inhibition coupled with a very small equilibrium constant K_1 for initial phosphine adduct formation such that the metallacyclohexane is not detectable by NMR ($K_1K_2 \ll 1$). While we cannot rule out this scenario, the participation of $L_2L'Pt^+{-}O^-$ species is the simplest explanation for the platinum carbonate exchange and redox reactions reported here.

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Supporting Information Available: Text giving additional experimental details (2 pages). Ordering information is given on any current masthead page.

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