Synthesis, characterization, and reactivity of a platinum(0) dimer: Pt2(.mu.-CO)(CO)2(.mu.-dppm)2

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Synthesis, Characterization, and Reactivity of a Platinum(0) Dimer: $Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$

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Summary: The zerovalent platinum dimer $[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]$ *(1) (dppm =* $Ph_2PCH_2PPh_2$*) has been prepared from* $[Pt_2Cl_2(\mu\text{-dppm})_2]$ *(2) via sodium borohydride reduction under carbon monoxide and from* $[Pt_2(\mu\text{-dppm})_3]$ *(3) by substitution of a dppm ligand with CO. This latter reaction is readily reversible and can undergo several cycles of carbonylation–decarbonylation. Complex 1 undergoes typical oxidative addition reactions; it is readily protonated to yield* $[Pt_2(H)(CO)(\mu\text{-dppm})_2](p\text{-}CH_3C_6H_4SO_3)\cdot C_6H_6$ *(4). With* I_2*, 1 reacts to yield* $[Pt_2I_2(\mu\text{-dppm})_2]$ *(5), and reaction with* CH_3I *produces* $[Pt_2(\mu\text{-}I)(CH_3)_2(\mu\text{-dppm})_2]I$ *(6).*

Platinum(0) phosphine complexes[2] and platinum dimers[3] have recently received much attention because of their interesting reaction chemistry and their potential as homogeneous catalysts. $[Pt_2(\mu\text{-dppm})_3]$,[4] for example, has been found to catalyze the reduction of nitric oxide and molecular oxygen by carbon monoxide under mild conditions.[5] This compound has been used to catalyze the reduction of carbon dioxide in the presence of dimethylamine with molecular hydrogen to form *N,N*-dimethylformamide,[6] and it has also been employed for the production of hydrogen from water–DMF solutions.[7] Until now, only a few platinum(0) dimers have been isolated and characterized.[8] In this note, we wish to report the synthesis and reactions of a new zerovalent platinum dimer, $[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]$ (1).

Experimental Section

General Comments. The complexes $[Pt_2Cl_2(\mu\text{-dppm})_2]$[9] and $[Pt_2(\mu\text{-dppm})_3]$[4] were prepared by standard procedures. The ligand, 1,2-bis(diphenylphosphino)methane, was purchased from Strem Chemicals. All manipulations were performed under a N_2 atmosphere using Schlenk techniques. ^1H NMR, $^{13}C\{^1H\}$ NMR, $^{31}P\{^1H\}$ NMR, and $^{195}Pt\{^1H\}$ NMR were recorded on a Bruker AC/E-200 FT-NMR between 25 and −87 °C. ^1H NMR, $^{13}C\{^1H\}$ NMR, $^{31}P\{^1H\}$ NMR, and $^{195}Pt\{^1H\}$ NMR chemical shifts were referenced to TMS, 85% H_3PO_4, and H_2PtCl_6, respectively. When possible, coupling constants and chemical shifts are reported as measured directly from the experimental spectra. In all other cases, the values listed are those determined using spectral simulations. IR spectra were recorded on a Mattson 4020 FT-IR spectrometer. Microanalyses were carried out by Atlantic Microlab, Inc., Norcross, GA.

1. Synthesis of $[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]$[10] (1) from $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (2). $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (0.303 g, 0.247 mmol) was added to 30 mL of anhydrous methanol, yielding a yellow suspension. Carbon monoxide was then bubbled through the suspension. Within 5–10 min, the suspension became a transparent yellow solution. The solution was filtered to remove any undissolved material, and $NaBH_4$ (0.133 g, 3.52 mmol), dissolved in 15 mL of absolute ethanol, was added to the filtrate over a period of 15 min with vigorous CO bubbling. A yellow suspension resulted. The yellow solid (1) was filtered under N_2, washed with 10 mL of CO purged methanol, and dried *in vacuo*. Yield: 0.267 g (87%). Anal. Calc for $C_{53}H_{44}O_3P_4Pt_2$: C, 51.16; H, 3.54. Found: C, 50.99; H, 3.51. Mp: 123 °C dec. IR (KBr): 1969, 1954 (ν_{CO}, terminal) and 1785 cm^{-1} (ν_{CO}, bridging). ^1H NMR (CD_2Cl_2, −43 °C): δ 2.08 (m, CH_2), $^3J_{Pt-H}$ = 29.6 Hz, $^2J_{P-H}$ = 6.1 Hz, δ 4.40 (m, CH_2), $^3J_{Pt-H}$ = 62.8 Hz, $^2J_{P-H}$ = 6.0 Hz, δ 6.71–7.61 (m, C_6H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ^{13}CO enriched, −87 °C): δ 184.4 (q, terminal CO), $^1J_{Pt-C}$ = 2083 Hz, $^2J_{Pt-C}$ = 143 Hz, $^2J_{P-C}$ = 6.6 Hz, δ 204.3 (q, bridging CO), $^1J_{Pt-C}$ = 939 Hz, $^2J_{P-C}$ = 17.8 Hz. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −43 °C): δ −0.15 (s), $^1J_{Pt-P}$ = 2957 Hz, $^2J_{Pt-P}$ = −9.1 Hz, $^2J_{P-P}$ = 58.0 Hz, $^3J_{P-P}$ = 227.5 Hz, $^3J_{P-P}$ = 10.7 Hz, $^1J_{Pt-Pt}$ = 1545.7 Hz. $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2, −53 °C): δ −4670.5 (t).

2. Synthesis of $[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]$ (1) from $[Pt_2(\mu\text{-dppm})_3]$ (3). To 10 mL of degassed benzene was added 0.085 g (0.054 mmol) of **3**. The solution was stirred, and a deep red solution resulted. CO was then bubbled through the solution. Over a period of 2 min, the solution color changed from red to yellow-orange. Slow addition of 50 mL of nitrogen purged hexanes afforded a yellow-orange precipitate which was filtered under nitrogen. The solid was washed with methanol (10 mL) and diethyl ether (10 mL). Yield: 0.043 g (62%). The analytical data obtained for compound 1 by this procedure were identical to the one described above.

3. Reaction of $[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]$ (1) with dppm. To 10 mL of degassed benzene was added 0.150 g (0.121 mmol) of 1. The resulting orange suspension was stirred, and 0.0464 g (0.121 mmol) of dppm was added. Over a period of 20 min, the orange suspension changed to a deep red solution. Degassed hexanes (35 mL) were added to this solution producing a red suspension. The red solid was filtered (0.110 g, 60%) under nitrogen and dried *in vacuo*. The product was found by ^1H and

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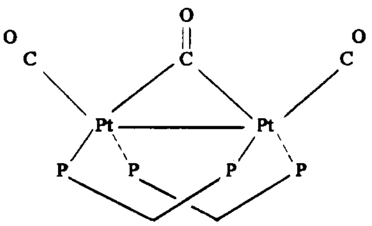

Figure 1. Proposed structure of $[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$.

$^{31}P\{^1H\}$ NMR spectroscopy to be the previously characterized $[Pt_2(\mu\text{-}dppm)_3]$[4] (3).

4. Reaction of $[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$ (1) with $p\text{-}CH_3C_6H_4SO_3H{\cdot}H_2O$. To 35 mL of CO purged benzene was added 0.116 g (0.0933 mmol) of 1. The resulting orange solution was stirred, and 0.018 g (0.0946 mmol) of $p\text{-}CH_3C_6H_4SO_3H{\cdot}H_2O$ was added. Within a few minutes, a yellow precipitate (4) started to form. The suspension was filtered (0.126 g, 93%), washed with benzene and hexanes, and dried *in vacuo*. Anal. Calc for $C_{64}H_{58}O_4P_4Pt_2S$: C, 53.44; H, 4.04. Found: C, 53.33; H, 4.10. Mp: 145 °C dec. IR (KBr): 2031 cm^{-1} (terminal CO). ^1H NMR (CD_2Cl_2, 24 °C): δ –6.82 (m, PtH), $^1J_{Pt-H} = 987$ Hz, $^2J_{Pt-H} = 50.9$ Hz, $^2J_{P-H} = 17.5$ Hz, $^3J_{P-H} = 8.1$ Hz, δ 2.22 (s, CH_3), δ 5.17 (m, CH_2), $^3J_{Pt-H} = 74.9$ Hz, $^2J_{P-H} = 3.6$ Hz, δ 6.9–7.7 (m, C_6H_5 and C_6H_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ^{13}CO enriched, 24 °C): δ 188.6 (q, terminal CO), $^1J_{Pt-C} = 1116$ Hz, $^2J_{Pt-C} = 194$ Hz, $^2J_{P-C} = 4.4$ Hz. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 24 °C): $\delta(P_A)$ 7.8, $^1J_{Pt-P} = 3346$ Hz, $^2J_{Pt-P} = 10.6$ Hz, $^2J_{P-P} = 58.9$ Hz, $^3J_{P-P} = 26.2$ Hz, $\delta(P_B)$ 11.2, $^1J_{Pt-P} = 2802$ Hz, $^2J_{Pt-P} = 81.6$ Hz. $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2, 24 °C): $\delta(Pt_A)$ –4435, $^1J_{Pt-P} = 3346$ Hz, $^2J_{Pt-P} = 9.6$ Hz, $\delta(Pt_B)$ –4732, $^1J_{Pt-P} = 2799$ Hz, $^2J_{Pt-P} = 84.3$ Hz, $^1J_{Pt-Pt} = 2440$ Hz.

5. Reaction of $[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$ (1) with I_2. To 15 mL of CO purged benzene was added 0.100 g (0.0804 mmol) of 1. The resulting yellow-orange solution was stirred, and 0.0212 g (0.0805 mmol) I_2 was added. Within a few minutes, a yellow precipitate (5) started to form. The suspension was filtered (0.098 g, 86%), washed with benzene and hexanes, and dried *in vacuo*. The product was found by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy to be the previously characterized $[Pt_2I_2(\mu\text{-}dppm)_2]$.[9]

6. Reaction of $[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$ (1) with CH_3I. To 15 mL of CO purged benzene was added 0.100 g (0.0804 mmol) of 1. The resulting yellow-orange solution was stirred, and 1 mL (16.1 mmol) CH_3I was added. After 2 h, a yellow precipitate (6) had formed. The suspension was filtered (0.083 g, 70%), washed with benzene and hexanes, and dried *in vacuo*. Anal. Calc for $C_{52}H_{50}I_2P_4Pt_2$: C, 43.27; H, 3.47. Found: C, 43.55; H, 3.32. ^1H NMR (CD_2Cl_2, 24 °C): δ 0.55 (t, CH_3), $^2J_{Pt-H} = 85.1$ Hz, $^3J_{P-H} = 6.6$ Hz, δ 4.49 (m, CH_aH_b), $^3J_{Pt-H} = {\sim}0$ Hz, $^2J_{P-H} = 6.2$ Hz, δ 5.04 (m, CH_aH_b), $^3J_{Pt-H} = 53.4$ Hz, $^2J_{P-H} = 3.2$ Hz, $^2J_{H-H} = 14.1$ Hz, δ 6.9–8.1 (m, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 24 °C): δ 11.1 (s), $^1J_{Pt-P} = 2944$ Hz, $^2J_{Pt-P} = 35.7$ Hz, $^3J_{P-P} = 32.8$ Hz, $^3J_{P-P} = 4.1$ Hz, $^1J_{Pt-Pt} = 408$ Hz. $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2, 24 °C): –4794 (t).

Results and Discussion

Reaction of $[Pt_2Cl_2(\mu\text{-}dppm)_2]$ with CO in methanol yields the known complex $[Pt_2(CO)(Cl)(\mu\text{-}dppm)_2]Cl$.[11] Reduction of this solution with $NaBH_4$ under CO affords a novel yellow-orange compound formulated as $[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$, in which two metal atoms are bridged by two diphosphine ligands and one carbon monoxide molecule (Figure 1). This platinum dimer is formulated as a complex with both platinum atoms in a zero oxidation state with a platinum–platinum bond, each metal having an 18-electron valence shell. The $^{31}P\{^1H\}$ NMR spectrum of 1 is described as an AA′A″A‴XX′ spin system (Figure 2). The presence of a platinum–platinum bond in the complex is confirmed by the magnitudes of the $^3J_{P-P}$ (10.7 Hz) and the $^2J_{Pt-P}$ (–9.1 Hz) coupling constants. The reported values are consistent with coupling constants obtained for triply bridged platinum dimers with a platinum–platinum bond.[12] The two bond Pt–P coupling constant and the two bond P–P coupling constant also appear to give some geometric information. Small negative two bond Pt–P coupling constants are found for complexes in which the two dppm ligands adopt the so-called W-frame structure,[13] while two bond P–P coupling constants fall in the range 50–120 Hz for complexes with PPtP angles of 90–120°.[4c] The relevant coupling constants for 1 seem to imply that this complex has the two diphosphine ligands *cis* to each other.

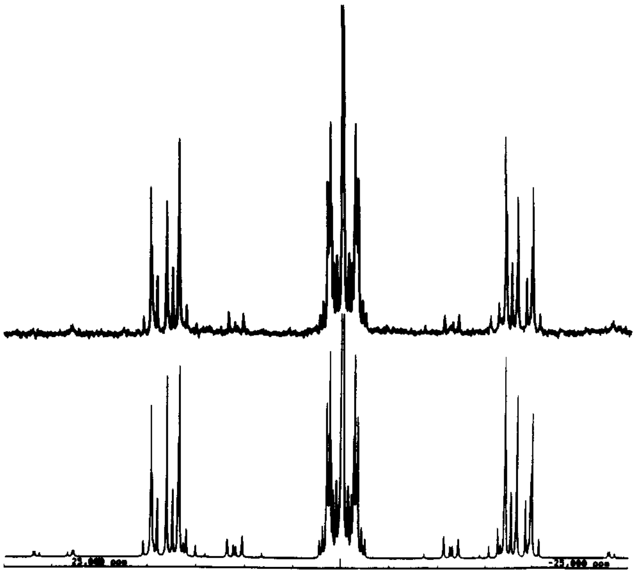

Figure 2. $^{31}P\{^1H\}$ NMR spectrum (upper trace) and computer simulation (lower trace) of $[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$ at –43 °C.

An alternate method for the preparation of complex 1, albeit in lower yields, involves the substitution of one dppm ligand with 3 molar equiv of CO (eq 1).

$$[Pt_2(\mu\text{-}dppm)_3] + 3CO \rightleftarrows [Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2] + dppm \quad (1)$$

The IR spectrum of complex 1 exhibits absorption bands attributable to coordinated carbon monoxide (terminal and bridging) as well as to diphosphine ligands. In the solid state, the compound is diamagnetic and thermally stable (mp 180 °C *in vacuo*), but sensitive to air. Solutions of 1 are very reactive toward oxygen. Exposure to air in the solid state results in a darkening of the color of the complex, a decrease of the intensities of the carbonyl bands, and the appearance of a new absorption in the IR at 837 cm^{-1}, which is indicative of the stretching vibration of a platinum peroxo complex, similar to the one reported for $Pt(O_2)(PPh_3)_2$.[14] 1 is most soluble in DMF and DMSO, moderately soluble in benzene and toluene, and insoluble in polar solvents. In chlorinated hydrocarbons, $[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$ is slowly oxidized to yield $[Pt_3(\mu\text{-}$

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$CO)(\mu\text{-dppm})_3]Cl_2$ as the main oxidation product.[15] A similar oxidation in a halocarbon solvent[16] has also been reported for the isoelectronic nickel complex, $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]$.[17]

$[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]$ does not react at room temperature with additional CO; the analogous nickel dimer, on the other hand, is known to react further with CO to form $[Ni_2(CO)_4(\mu\text{-dppm})_2]$[18] and $Ni(CO)_3(\eta^1\text{-dppm})$.[18]

With dppm, **1** undergoes a fast reaction to yield a red solution from which $[Pt_2(\mu\text{-dppm})_3]$ (**3**) can be precipitated (eq 2). IR analysis of this product shows that the bridging as well as the terminal carbonyl bands have disappeared.

$$[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2] + \text{dppm} \rightleftarrows [Pt_2(\mu\text{-dppm})_3] + 3CO \quad (2)$$

This reaction is readily reversible by reintroducing CO into the solution. The decarbonylation–carbonylation cycle, which is accompanied by color changes (yellow ⇄ red) and monitored by NMR, can be repeated several times on the same reaction mixture.

$[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]$ readily undergoes oxidative addition reactions. Complex **1** can be protonated with *p*-toluenesulfonic acid to yield a lemon yellow solid, $[Pt_2(H)(CO)(\mu\text{-dppm})_2](p\text{-}CH_3C_6H_4SO_3)\cdot C_6H_6$ (**4**) (eq 3).

$$[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2] + p\text{-}CH_3C_6H_4SO_3H \rightarrow [Pt_2(H)(CO)(\mu\text{-dppm})_2](p\text{-}CH_3C_6H_4SO_3) + 2CO \quad (3)$$

The infrared spectrum shows a single terminal carbonyl band at 2031 cm^{-1}, while the terminal hydride is revealed in the ^1H NMR spectrum (−6.82 ppm). Further evidence for the presence of nonequivalent ligands on the two platinum atoms is furnished by a rather complex $^{31}P\{^1H\}$ NMR spectrum. This spectrum is best described as an AA′BB′ spectrum superimposed with spectra due to AA′BB′X and AA′BB′Y. The benzene molecule of crystallization is confirmed by ^1H NMR. The IR, $^{31}P\{^1H\}$ NMR, and ^1H NMR data for complex **4** are similar to the data obtained for the previously reported complex, $[Pt_2(H)(CO)(\mu\text{-dppm})_2]PF_6$.[19]

With I_2, **1** reacts to yield quantitatively $[Pt_2I_2(\mu\text{-dppm})_2]$[9] (**5**) (eq 4). Reaction with CH_3I yields $[Pt_2(\mu\text{-}I)(CH_3)_2(\mu\text{-dppm})_2]I$ (eq 5). The $^{31}P\{^1H\}$ and ^1H NMR data obtained for this complex are similar to the data obtained for $[Pt_2(\mu\text{-}I)(CH_3)_2(\mu\text{-dppm})_2]PF_6$.[20] In addition, ^1H and $^{31}P\{^1H\}$ NMR data suggest that in this latter reaction $[Pt_2(CO)(CH_3)(\mu\text{-dppm})_2]I$ is formed first followed by formation of **6**. Similar oxidative addition reactions have also been reported for other zerovalent dimers of platinum, $Pt_2(\mu\text{-dppm})_3$,[20] and palladium, $Pd_2(\mu\text{-dppm})_3$.[21]

$$[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2] + I_2 \rightarrow [Pt_2I_2(\mu\text{-dppm})_2] + 3CO \quad (4)$$

$$[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2] + 2CH_3I \rightarrow [Pt_2(\mu\text{-}I)(CH_3)_2(\mu\text{-dppm})_2]I + 3CO \quad (5)$$

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(15) The complex decomposes in the NMR tube at room temperature over several days. The main decomposition product has the following spectroscopic data: IR (KBr) 1757 cm^{-1} (bridging CO); ^1H NMR (CD_2Cl_2) δ 5.5–6.0 (m, CH_2), 7.0–8.5 (m, C_6H_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 24 °C) δ −11.6 (s), $^1J_{Pt-P} = 3713$ Hz, $^2J_{Pt-P} = -8.6$ Hz, $^3J_{P-P} = 169.9$ Hz, $^1J_{Pt-Pt} = 610$ Hz; $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2, 24 °C) δ −4300 (t), $^1J_{Pt-P} = 3712$ Hz, $^2J_{Pt-P} = -8.6$ Hz. These data are consistent with the coordinatively unsaturated trinuclear, triangular cluster $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$: Ferguson, G.; Lloyd, B. R.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 344.

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