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Article

Carbonyl Complexes of Platinum(0): Synthesis and Structure of $[(Cy_3P)_2Pt(CO)]$ and $[(Cy_3P)_2Pt(CO)_2]$

Stefanie Bertsch, Holger Braunschweig,* Melanie Forster, Katrin Gruss, and Krzysztof Radacki

Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

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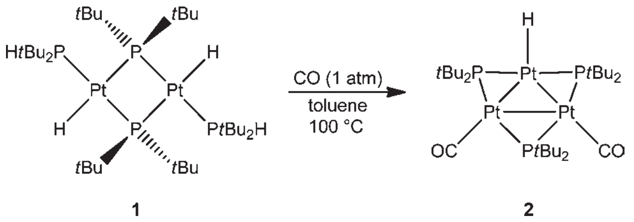
The platinum(0) monocarbonyl complex, $[(Cy_3P)_2Pt(CO)]$, was synthesized by reaction of $[(Cy_3P)_2Pt]$ with $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ and subsequent irradiation. X-ray structure analysis was performed and represents the first structural evidence of a platinum(0) monocarbonyl complex bearing two free phosphine ligands. Its corresponding dicarbonyl complex $[(Cy_3P)_2Pt(CO)_2]$ was synthesized by treatment of $[(Cy_3P)_2Pt]$ with CO at −40 °C and confirmed by X-ray structure analysis.

Introduction

Early work on platinum carbonyl complexes dates back to the late 1950s, when the search for well-defined carbonyl complexes of platinum(0) led to the discovery of numerous structural motifs.[1] As far as platinum(0) carbonyl complexes with phosphines as sole coligands are concerned, multinuclear clusters as well as monocarbonyl and dicarbonyl compounds are long known. A first outlook on phosphine derivatives of platinum(0) carbonyl complexes was given by Malatesta and Cariello[2] and further investigated by Booth, Chatt, and Chini.[3] Crystal structure determination of the clusters $[(Cy_3P)_3Pt_3(CO)_3]$[4] and $[(Cy_3P)_4Pt_3(CO)_3]$[5] followed a few years later. Numerous platinum carbonyl phosphine cluster types with a variety of compositions have been prepared since then.[6] An interesting system is the dinuclear species $[Pt_2(\mu\text{-}PtBu_2)_2(H)_2(PtBu_2H)_2]$ (**1**) which converts to $[Pt_3(\mu\text{-}PtBu_2)_3H(CO)_2]$ (**2**) under a CO atmosphere (Scheme 1). Treatment of **1** in the presence of an excess of phosphines led to the formation of the monocarbonyl derivatives $[(R_3P)_3Pt(CO)]$ ($R_3 = Ph_3, Et_3, tBu_2H$).[7]

Scheme 1. Synthesis of the Triangular Cluster **2**



Low-temperature treatment of $[(Ph_3P)_3Pt]$ with CO at −80 °C also afforded $[(Ph_3P)_3Pt(CO)]$ (**3**), and subsequent warming to −65 °C resulted in the conversion to the spectroscopically characterized $[(Ph_3P)_2Pt(CO)_2]$.[8] To the best of our knowledge, the only structural evidence for a dicarbonyl phosphine platinum complex was provided in the case $[(EtPh_2P)_2Pt(CO)_2]$ (**4**).[9] A typical reaction pathway to obtain this species is the reductive elimination of a suitable leaving group from a platinum(II) center in the presence of CO.[10] Thus, the aforementioned dicarbonyl complex $[(Ph_3P)_2Pt(CO)_2]$ is also accessible by reaction of $[(Ph_3P)_2Pt(H)Cl]\cdot EtOH$ with CO.[11]

The known platinum monocarbonyl compounds incorporate either three phosphines or chelating bis(phosphine) ligands. $[(Ph_3P)_3Pt(CO)]$ (**3**), reported by Bellon et al. in 1969, represents the first structural characterization of this type of compound.[12]

Chelating phosphine ligands were important for the synthesis of platinum monocarbonyl complexes bearing only two phosphine centers. The reaction of $[(dfepe)Pt(\mu\text{-}H)]_2$

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*To whom correspondence should be addressed. E-mail: h.braunschweig@mail.uni-wuerzburg.de. Fax: +49-(0)931/31-84623. Tel: +49-(0)931/31-85260.

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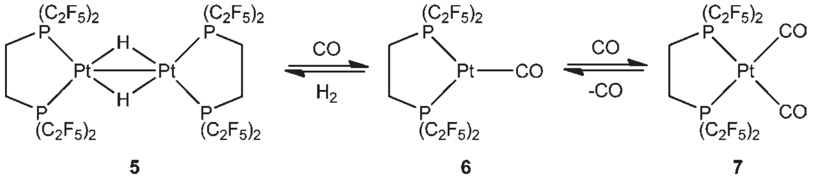
Scheme 2. Reaction of **5** with CO



(dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$) (**5**) with CO gave access to both the mono- and dicarbonyl products **6** and **7**, though **7** could not be isolated due to the facile loss of CO (Scheme 2). However, neither complex could be characterized in the crystal.[13]

The same group showed that, in addition to Pt(0) systems, cationic (fluoroalkyl)phosphine Pt(II) mono- and dicarbonyl complexes are also accessible.[14]

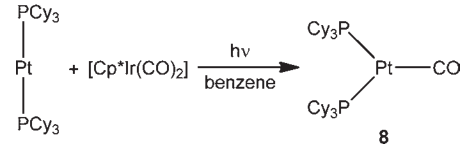
The synthesis of monocarbonyl platinum complexes was motivated by our search for suitable precursors for borylene−carbonyl exchange reactions, thus allowing for the synthesis of platinum(0)borylene complexes. Despite the rather well-developed chemistry of borylene complexes,[15] corresponding mononuclear species deriving from platinum are still restricted to only two examples, which display platinum in the formal oxidation state of +II.[16]

Herein we present the synthesis and structural characterization of $[(Cy_3P)_2Pt(CO)]$ (**8**), the first platinum monocarbonyl complex with two nonchelating phosphine ligands and the platinum dicarbonyl complex $[(Cy_3P)_2Pt(CO)_2]$ (**9**).

Results and Discussion

The title compounds were synthesized via two different reaction pathways. The synthesis of $[(Cy_3P)_2Pt(CO)]$ (**8**) required treatment of $[(Cy_3P)_2Pt]$ with $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ as a selective source for 1 equiv of CO under photolytic conditions, whereupon one carbonyl ligand is transferred from the iridium to the platinum center.

Scheme 3. Formation of the Platinum Monocarbonyl Complex **8**



After workup, the monocarbonyl complex **8** is isolated as an orange crystalline material in 31% yield. The ^{31}P NMR spectrum reveals a signal at 63.7 ppm similar to that of the starting material $[(Cy_3P)_2Pt]$ (62.3 ppm, $^1J_{P-Pt}$ = 4160 Hz), with a marginally lower coupling constant of $^1J_{P-Pt}$ = 4101 Hz. The crystal structure of **8** revealed a C_{2v} symmetric molecule displaying a trigonal-planar coordinated platinum center with a P1−Pt−P1_a angle of 124.0(9) Å.[17]

To the best of our knowledge, compound **8** represents the first structurally characterized complex of the composition $[(R_3P)_2Pt(CO)]$. In comparison to the four-coordinated tris(phosphine) carbonyl complex **3**, which displays Pt−C distances of 1.86(3) and 1.84(2) Å, due to the presence of two polymorphs, the three-coordinate bis(phosphine) complex **8** exhibits a very similar Pt−C separation of 1.885(12) Å.[12,18] Likewise, the C−O bond lengths are in the same range that is 1.139(7) and 1.12(4) Å for **3** and 1.131(18) Å for **8**.

An effort to generate the corresponding platinum(0) dicarbonyl complex $[(Cy_3P)_2Pt(CO)_2]$ (**9**) was achieved via a different synthetic approach. A toluene solution of $[(Cy_3P)_2Pt]$ was briefly exposed to CO at temperatures below −20 °C to afford a bright yellow solution. The product is formed as confirmed by a ^{31}P NMR signal at 21.2 ppm with a coupling constant of $^1J_{P-Pt}$ = 3138 Hz.

A similar synthetic route based on the treatment of $[(Cy_3P)_2PtH_2]$ with CO at room temperature was reported in 1979. A new resonance at 19.8 ppm was observed in the ^{31}P NMR spectra, but attempts to isolate the product only resulted in the cluster $[(Cy_3P)_3Pt_3(CO)_3]$.[19] Later work of the same group described the reaction of *trans*-$[(Cy_3P)_2PtH_2]$ with CO at low temperature that succeeded in the formation of **9**, which was spectroscopically characterized.[20] We were able to isolate the dicarbonyl compound $[(Cy_3P)_2Pt(CO)_2]$ (**9**) as a yellow solid in 71% yield upon concentration of the reaction mixture at low temperatures. Colorless crystals suitable for X-ray structure determination were obtained from toluene solutions after 7 days at −30 °C. In the crystal, **9** displays a

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[17] The crystal data of **8** were collected at a Bruker X8Apex diffractometer with a CCD area detector and multilayer mirror monochromated Mo Kα radiation. The crystal data of **9** were collected at a Bruker D8 diffractometer with an Apex CCD area detector and graphite monochromated Mo Kα radiation. The structures were solved using direct methods, refined with the Shelx software package (Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. Crystal data for 8: $C_{37}H_{66}OP_2Pt$, M_r = 783.93, orange plate, 0.27 × 0.17 × 0.07 mm^3, monoclinic space group *C*2/*c*, *a* = 16.7337(12) Å, *b* = 9.1857(7) Å, *c* = 24.2468(17) Å, β = 109.375(3)°, *V* = 3515.9(4) Å^3, *Z* = 4, ρ_{calcd} = 1.481 g cm^{-3}, μ = 4.109 mm^{-1}, *F*(000) = 1616, *T* = 100(2) K, R_1 = 0.0314, wR^2 = 0.0725, 5214 independent reflections [$2\theta \le 65.5°$] and 187 parameters. Crystal data for 9: $C_{45}H_{74}O_2P_2Pt$, M_r = 904.07, colorless block, 0.19 × 0.38 × 0.44 mm^3, orthorhombic space group *Pna*2$_1$, *a* = 26.531(2) Å, *b* = 10.7170(9) Å, *c* = 15.0153(13) Å, *V* = 4269.3(6) Å^3, *Z* = 4, ρ_{calcd} = 1.407 g cm^{-3}, μ = 3.396 mm^{-1}, *F*(000) = 1872, *T* = 173(2) K, R_1 = 0.0195, wR^2 = 0.0397, 10 706 independent reflections [$2\theta \le 56.9°$] and 452 parameters. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-795251 (8) and CCDC-795252 (9). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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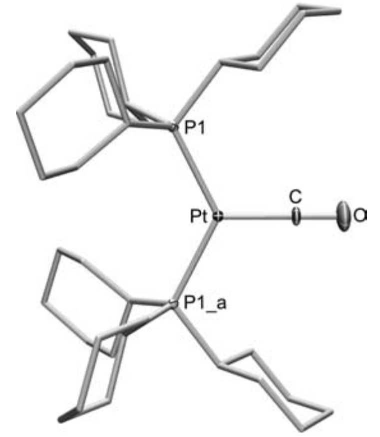
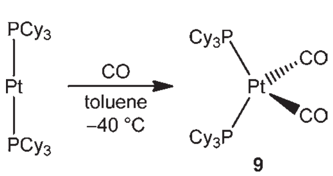


Figure 1. Molecular structure of **8** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Symmetry-related positions ($-x$, y, $-z + 1/2$) are denoted by the suffix _a. Selected bond lengths [Å] and angles [deg]: Pt−C 1.885(12), C−O 1.131(18); P1−Pt−P1_a 124.0(9).

Scheme 4. Synthesis of the Platinum Dicarbonyl Complex **9**



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distorted tetrahedral geometry of the platinum center with a P1−Pt−P2 angle of 116.62(2)°, which is somewhat more acute than the corresponding angle in complex **8** (124.0(9)°). However, in the only other structurally characterized bisphospine dicarbonyl complex of platinum, that is [$(EtPh_2P)_2Pt(CO)_2$] (**4**),[9b] the phosphine ligands include a much smaller angle of only 97.9(2)°. Besides this difference, further important structural data such as the Pt−C (**9**: 1.920(3) and 1.897(3) Å; **4**: 1.92(2) Å) and C−O distances (**9**: 1.139(4) and 1.143(4) Å; **4**: 1.14(2) Å) are comparable.

As reported earlier (vide supra), the dicarbonyl complex **9** proved to be stable, both in solution and in the solid state, only at temperatures below −20 °C. Thus, a bright yellow solution of **9** turns immediately red upon warming to room temperature with formation of the trinuclear clusters [$(Cy_3P)_4Pt_3(CO)_3$] and [$(Cy_3P)_3Pt_3(CO)_3$], as indicated by ^{31}P NMR signals at 69.8 ppm for the latter and X-ray structure analyses.[21] Likewise, direct treatment of the platinum precursor [$(Cy_3P)_2Pt$] with CO at room temperature afforded a red solution and the aforementioned platinum clusters. This finding is quite surprising as it significantly differs from that of other platinum phosphine carbonyls such as **6** and **7** (vide supra). Moreover, it already indicates that degradation of **9** to the trinuclear cluster species proceeds via initial loss of a PCy_3 ligand. In the case of liberation of CO from **9** one would have to expect exclusive formation of the aforementioned complex **8**, which proved to be thermally stable at room temperature.

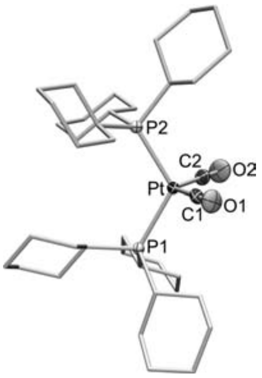

Figure 2. Molecular structure of **9** (thermal ellipsoids at the 50% probability level). One molecule of toluene and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pt−C1 1.920(3), Pt−C2 1.897(3), C1−O1 1.139(4), C2−O2 1.143(4); P1−Pt−P2 116.62(2).

According to former calculations, borylene ligands are better sigma donors than CO ligands and therefore capable of forming a stronger bond with transition metals.[22] Based on these bonding properties, various transition metal borylene complexes have been prepared in our group in the past decade by means of intermetallic borylene transfer reactions, by treating transition metal carbonyl complexes with aminoborylene complexes [$(OC)_5M{=}BN(SiMe_3)_2$] (M = Cr, Mo, W).[15b,23] Compound **8** has been examined for thermally and photochemically induced borylene transfer by treatment with equimolar amounts of [$(OC)_5Mo{=}BN(SiMe_3)_2$] and [$(OC)_5Cr{=}BN(SiMe_3)_2$], respectively. However, the detected ^{11}B and ^{31}P NMR signals do not suggest the formation of a terminal platinum borylene complex [$(Cy_3P)_2Pt{=}BN(SiMe_3)_2$]. Instead, **8** releases a PCy_3 ligand under these conditions, which reacts with [$(OC)_5Mo{=}BN(SiMe_3)_2$] resulting in *trans*-[$(Cy_3P)(OC)_4Mo{=}BN(SiMe_3)_2$] ($^{31}P$: δ = 51.2 ppm; ^{11}B: δ = 92 ppm) and with [$(OC)_5Cr{=}BN(SiMe_3)_2$] yielding *trans*-[$(Cy_3P)(OC)_4Cr{=}BN(SiMe_3)_2$] ($^{31}P$: δ = 64.7 ppm; ^{11}B: δ = 96 ppm).[23a] In the former case, after heating for 2 h at 80 °C, additional ^{31}P NMR signals (^{31}P: δ = 71.1, 47.6 ppm) can be observed that suggest the formation of a semibridging molybdenum borylene species due to similar NMR values.[24]

Conclusion

In conclusion, we have reported the first structural characterization of a platinum(0) monocarbonyl complex with two nonchelating phosphine ligands, [$(Cy_3P)_2Pt(CO)$] (**8**). The corresponding dicarbonyl compound [$(Cy_3P)_2Pt(CO)_2$] (**9**) has provided a rare structural evidence for this class of compound.

Experimental Section

All manipulations were performed in an inert atmosphere of argon using standard Schlenk and glovebox techniques.

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Solvents were distilled over alkali metal, degassed, and stored over molecular sieves (4 Å) under argon. Deuterated solvents were degassed by three freeze−pump−thaw cycles and stored under argon over molecular sieves. $[(Cy_3P)_2Pt]$[25] and $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$[26] were prepared according to known methods.

NMR experiments were performed on a Bruker Avance 500 (^{1}H: 500.1 MHz; ^{31}P: 202.5 MHz; ^{13}C: 125.8 MHz) apparatus. ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra were calibrated to TMS; in the case of $^{31}P\{^1H\}$ NMR spectra 85% H_3PO_4 was used as external standard. Elemental analyses were performed on an Elementar Vario Micro Cube elemental analyzer.

Synthesis of $[(Cy_3P)_2Pt(CO)]$ (8). $[(Cy_3P)_2Pt]$ (0.022 g, 0.029 mmol) was added to a pale yellow solution of $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ (0.011 g, 0.029 mmol) in benzene (1.0 mL). The intensely yellow solution was kept at room temperature for 24 h and then irradiated for 18 h. The resulting dark orange solution was layered with hexane, and orange crystals were obtained after 3 days. The crystals were washed thoroughly with hexane (10 × 0.5 mL) until the washing solution remained colorless (0.007 g, 31%). ^{1}H NMR (500.1 MHz, d_8-tol): $\delta = 2.07-1.11$ (m, 66H, Cy) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, d_8-tol): $\delta = 38.61$ (m, C^1, Cy), 30.93 (br s, C^3, C^5, Cy), 28.05 (m, C^2, C^6, Cy), 26.98 ppm (s, C^4, Cy). $^{31}P\{^1H\}$ NMR (202.5 MHz, d_8-tol): $\delta = 63.7$ ($^1J_{P-Pt} =$ 4101 Hz) ppm. IR: 1916 cm^{-1}. Elemental analysis (%) calculated for $C_{37}H_{66}OP_2Pt$ (783.95): C 56.69, H 8.49; found: C 56.94, H 8.40.

Synthesis of $[(Cy_3P)_2Pt(CO)_2]$ (9). A solution of $[(Cy_3P)_2Pt]$ (0.050 g, 0.066 mmol) in toluene (2.0 mL) was cooled to −40 °C. The bright yellow solution was treated for 1 s with CO and darkened. The reaction mixture turned red within 10 min above 0 °C and yielded the Pt_3 cluster $[(Cy_3P)_3Pt_3(CO)_3]$. Isolation of **9** was possible if the solvent of the intensely yellow solution was removed at −15 to −35 °C (0.038 g, 71%). As the resulting yellow solid was unstable at room temperature, no further IR data and elemental analysis could be obtained. Colorless crystals suitable for X-ray structure analysis were obtained from the toluene solution after 7 days at −30 °C. ^{1}H NMR (500.1 MHz, d_8-tol): $\delta = 2.04-1.18$ (m, 66H, Cy) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, d_8-tol): $\delta = 37.78$ (virtual triplet, N[27] = 24 Hz, C^1, Cy), 31.61 (s, C^3, C^5, Cy), 28.00 (virtual triplet, N[28] = 16 Hz, C^2, C^6, Cy), 27.00 ppm (s, C^4, Cy). $^{31}P\{^1H\}$ NMR (202.5 MHz, d_8-tol): $\delta = 21.2$ ($^1J_{P-Pt} = 3138$ Hz) ppm.

Acknowledgment. We thank the DFG for financial support.

Supporting Information Available: CIF files giving X-ray structural data of **8** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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