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Synthesis and Characterization of Cationic Dinuclear Hydridoplatinum Complexes: Crystal and Molecular Structure of $[Pt_2(\mu\text{-}H,\mu\text{-}CO)(dpe)_2][BF_4]$ (dpe = 1,2-Bis(diphenylphosphino)ethane)

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Reaction of $[Pt_2H_3(L\text{-}L)_2][A]$, L-L = $Ph_2P(CH_2)_2PPh_2$ (dpe), $Ph_2P(CH_2)_3PPh_2$ (dpp), or $Ph_2P(CH_2)_4PPh_2$ (dpb), A = BF_4 (**a**) or I (**b**), with CO or CNR leads to displacement of dihydrogen and formation of the corresponding salts of $[Pt_2H(L')(L\text{-}L)_2]^+$: **1a** or **1b**, L-L = dpe, L′ = CO; **2a**, L-L = dpp, L′ = CO; **3a**, L-L = dpb, L′ = CO; **4a** or **4b**, L-L = dpe, L′ = $CNCH_3$; **5a** or **5b**, L-L = dpe, L′ = $CNC_6H_4\text{-}p\text{-}CH_3$; **6a**, L-L = dpe, L′ = $CNCMe_3$. The infrared absorptions of the cations $\mathbf{1}^+$–$\mathbf{5}^+$ are consistent with the presence of a bridging carbonyl or isocyanide ligand. For $\mathbf{6}^+$, however, infrared evidence suggests that the hydrogen atom and the $CNCMe_3$ group are terminally bonded. At 213 K limiting ^1H and ^{31}P NMR spectra of the cation $\mathbf{3}^+$ indicate the hydrogen to be coupled to two phosphorus nuclei in trans and two in cis positions. At room temperature the spectra indicate fluxional behavior with rapid exchange of the phosphorus atom positions with respect to the bridging hydrogen atom. Crystal and molecular structure determination of **1a** was undertaken at 115 K, confirming a bridging position each for the hydrogen atom and for the carbonyl group. The salt crystallizes in the monoclinic space group $P2/n$ with the following cell dimensions: a = 13.477 (5), b = 11.090 (4), c = 15.976 (8) Å; β = 97.40 (3)°. There are two $[Pt_2(\mu\text{-}H,\mu\text{-}CO)(dpe)_2]^+$ cations and two BF_4^- anions per unit cell. The cation possesses crystallographically imposed C_2 symmetry. The bidentate phosphine groups are chelated each to a separate metal atom. The coordination around each metal atom is close to a square plane consisting of two cis-coordinated phosphorus atoms, the bridging hydrogen atom, and the carbon of the bridging CO group. The Pt–Pt distance (bridged by hydrogen and CO) is 2.716 (1) Å with Pt–C_μ and Pt–H_μ at 2.018 (1) and 1.55 (4) Å, respectively.

Introduction

As part of our studies[2-4] of the dinuclear trihydrido cationic complexes of platinum,[5-7] we examined their reaction with CO and with isocyanides and determined the structure for one of the resulting derivatives. This is the subject matter of this paper; a part of this work has been communicated in preliminary form.[2]

Results

The reaction of carbon monoxide with various L–L derivatives of the dinuclear trihydrido complexes was carried out by bubbling the gas through their acetone solutions at room temperature. Within a few minutes the solutions turn dark, and complexes **1a**, **2a**, or **3a** can be obtained in high yields. The iodide **1b** can be obtained from the tetrafluoroborate by exchange with KI in methanol; KBF_4 is insoluble in this medium.

Analytical data are given in Table I. These and the conductivity data are consistent with the formula representing displacement of dihydrogen by the incoming ligand. The reaction is not reversible at room temperature and atmospheric pressure; **1a** is unchanged in solution after several hours of exposure to bubbling dihydrogen.

The reactions with methyl and p-tolyl isocyanides were carried out with varying ratios of ligand to the dinuclear trihydrido complexes; upon addition of isocyanide to a solution of the trihydrides, a deep color develops, which fades to yellow by addition of excess ligand. The CNR:Pt ratio corresponding to the dark species was found to be 1:2; together with the analytical and infrared data (vide infra), a formula of $[Pt_2H(CNR)(L\text{-}L)_2][A]$ (**4a** and **5a**) is established. These complexes could also be obtained by reaction of the isocyanides with the corresponding CO derivatives, representing the typical displacement series for these complexes.[8]

Somewhat different results are observed with *tert*-butyl isocyanide; while a species of the same mole ratio (CNR:Pt = 1:2) is obtained, this is a yellow compound with a noticeably different IR spectrum (vide infra). Since the same species could be isolated by displacement of CO from salts of $[Pt_2H(CO)(L\text{-}L)_2]^+$, the possibility that the yellow compound was simply an adduct of the trihydrido cation could be excluded.

Spectra. For complexes **1a**–**5a**, the region around 2000 cm^{-1} is completely blank, ruling out the presence of terminal bonding for the hydrogen atom as well as for the carbonyl and isocyanide groups. This was confirmed by structure determination for **1a** in which a bridging position for the carbonyl group and the hydride ligand was ascertained (vide infra). Infrared spectra for derivatives **1a**–**5a** and their corresponding deuterated derivatives showed no significant differences, especially in the region around 1600 cm^{-1}, where the modes of bridging hydrogen could be expected[9] and where they have been observed in other derivatives.[4,10]

The significant feature of the infrared spectra of complexes **1a**–**5a** is a strong band around 1730 or 1650 cm^{-1} (see Table I) assigned respectively to a bridging carbonyl or a bridging

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Table I. Analytical and IR Spectral Data[a,d]

compd	color	mp/°C	% C	% H	% other	IR[e]
$[Pt_2(\mu\text{-H},\mu\text{-CO})(dpe)_2][BF_4]$ (**1a**)	turquoise-green	dec pt >225	48.71 (48.87)	3.65 (3.76)		1720 vs (Nujol) 1735 vs ($CHCl_3$)
$[Pt_2(\mu\text{-H},\mu\text{-CO})(dpe)_2][I]$ (**1b**)	green	dec pt >185	47.00 (47.41)	3.65 (3.65)	O 1.80 (1.19)	1720 vs (Nujol) 1735 vs ($CHCl_3$)
$[Pt_2(\mu\text{-D},\mu\text{-CO})(dpe)_2][BF_4]$ (**1a**-d_1)	turquoise-green		48.75 (48.82)	3.70 (3.84)		1720 vs (Nujol)
$[Pt_2(\mu\text{-H},\mu\text{-CO})(dpp)_2][BF_4]$ (**2a**)	violet	dec pt >120	49.47 (49.65)	4.07 (3.98)	F 5.51 (5.71)	1740 vs (Nujol) 1750 vs ($CHCl_3$)
$[Pt_2(\mu\text{-H},\mu\text{-CO})(dpb)_2][BF_4]$ (**3a**)	pink-violet	dec pt >150	50.35 (50.39)	4.35 (4.20)		1735 vs (Nujol)
$[Pt_2(\mu\text{-H},\mu\text{-CNCH}_3)(dpe)_2][BF_4]$ (**4a**)	pink-violet	ca. 205	50.50 49.32 (49.30)	3.90 4.06 (3.95)	N 1.00[b] 1.12[c] (1.06)	1665 m (Nujol) 1645 m (Nujol)
$[Pt_2(\mu\text{-H},\mu\text{-CNCH}_3)(dpe)_2][I]$ (**4b**)	pink	ca. 175	48.60 47.80 (47.84)	3.90 3.84 (3.84)	N 0.96[b] 0.86[c] (1.03)	1640 m (Nujol) 1665 m 1650 m (CH_2Cl_2)
$[Pt_2(\mu\text{-H},\mu\text{-CNC}_6H_4CH_3\text{-}p)(dpe)_2][BF_4]$ (**5a**)	dark violet	225–228	52.00 51.76 (51.79)	4.17 4.13 (4.02)	N 0.93[b] 0.82[c] (1.01)	1645 m (Nujol) 1660 s (CH_2Cl_2)
$[Pt_2(\mu\text{-H},\mu\text{-CNC}_6H_4CH_3\text{-}p)(dpe)_2][I]$ (**5b**)	dark violet	185	50.45 (50.34)	4.02 (3.91)	N 1.02 (0.98)	1640 s (Nujol) 1660 s (CH_2Cl_2)
$[Pt_2(\mu\text{-D},\mu\text{-CNC}_6H_4CH_3\text{-}p)(dpe)_2][BF_4]$ (**5a**-d_1)	dark violet		51.17 (51.75)	4.16 (4.09)	N 0.96 (1.00)	1645 m (Nujol) 1660 s (CH_2Cl_2)
$[PtH(dpe)Pt(CNC(CH_3)_3)(dpe)][BF_4]$ (**6a**)	yellow	dec pt >185	50.60 50.80 (50.43)	4.19 4.40 (4.27)	N 0.93[b] 1.00[c] (1.03)	2160 vs (Nujol) 1980 m (Nujol)
$[PtD(dpe)Pt(CNC(CH_3)_3)(dpe)][BF_4]$ (**6a**-d_1)	yellow		51.01 (50.39)	4.15 (4.34)	N 1.14 (1.03)	2160 vs (Nujol)

[a] Calculated values in parentheses. [b] Synthesized from the trihydrides. [c] Synthesized from the carbonyl complex. [d] Molecular weights: **1a**, 1250 in $CHCl_3$ (calcd 1302); **6a**, 1366 in $CHCl_3$ (calcd 1357). [e] ν(CO) or ν(CNR).

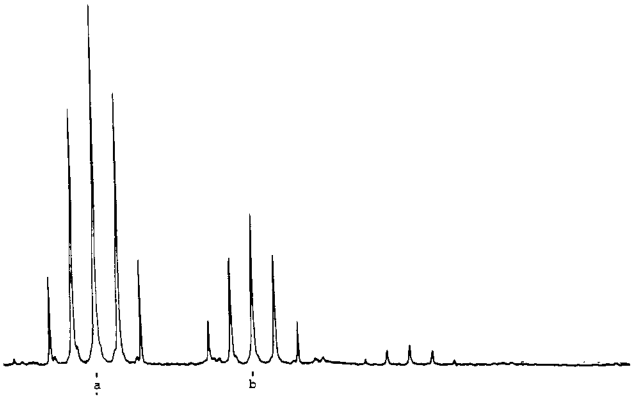


Figure 1. Upper field half of high-field Pt–H multiplet in the ^{1}H NMR ($CDCl_2$, 303 K) of $[Pt_2(\mu\text{-H},\mu\text{-CO})(dpb)_2][BF_4]$ (**3a**). The separation of peaks a and b is 224.5 Hz.

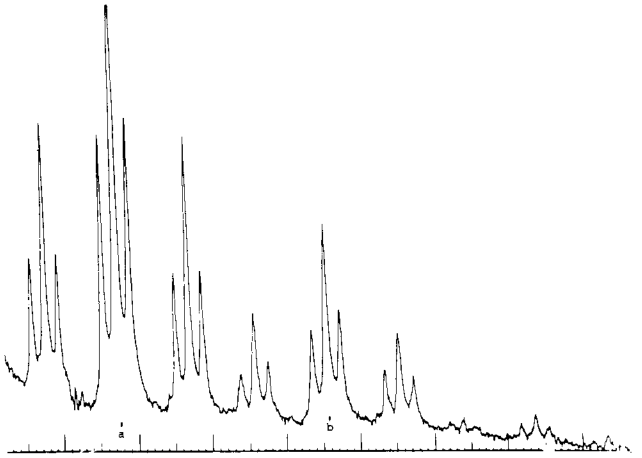


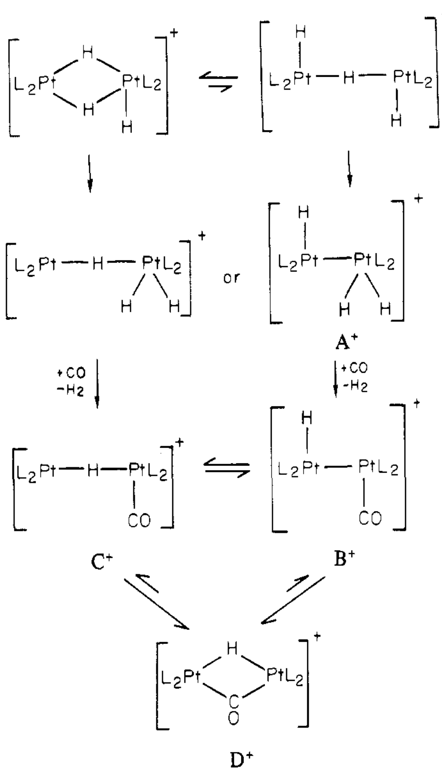
Figure 2. Upper field half of high-field Pt–H multiplet in the ^{1}H NMR ($CDCl_2$, 213 K) of $[Pt_2(\mu\text{-H},\mu\text{-CO})(dpb)_2][BF_4]$ (**3a**). The separation of peaks a and b is 224.5 Hz.

isocyanide group. These stretching frequencies are at somewhat lower wavenumbers than might be expected in a cationic complex, a point taken up again in a later discussion section.

By contrast, in the infrared spectrum of **6a**, bands at 2160 and 1995 cm^{-1} give evidence respectively that the isocyanide and the hydrido ligands are both terminally bonded. The assignment of the band at 1995 cm^{-1} is confirmed by its disappearance upon deuteration to give the complex **6a**-d_1. A corresponding Pt–D absorption is however not seen in **6a**-d_1 due to interference from absorptions due to the ligands.

The ^{1}H NMR spectrum of **3a** was well resolved and recorded at 303 and 213 K; see Figures 1 and 2. At 303 K the signal for the hydrido ligand consists of a quintet (relative intensity 1:8:18:8:1) of binomial quintets centered at τ 11.7 in CD_2Cl_2. The quintet pattern, ^1J(Pt–H) = 449 Hz, arises from the superposition of three subspectra due to the three isotopomeric combinations of platinum atoms that are possible in the dinuclear complex, i.e. Pt–Pt, ^{195}Pt–Pt, and ^{195}Pt–^{195}Pt (ca. 4:4:1), while the splitting of each signal into a binomial quintet is due to coupling to four equivalent phosphorus atoms, ^2J(P–H) = 32 Hz. Spectra of this type have been previously observed in other dinuclear species, e.g. in the trihydrides $[Pt_2H_3(L\text{-}L)_2]^+$,[2,4] and are indicative of the magnetic equivalence of the four phosphorus atoms and of the two platinum nuclei as a result of dynamic processes. These are observed over a narrow range of temperatures in the present case; below 290 K fluxionality gradually disappears, and at 213 K it is possible to obtain the limiting spectrum. At this temperature the spectrum consists of a quintet, ^1J(Pt–H) = 449 Hz, of triplets of triplets, ^2J(P–H) = 78 and 14.7 Hz, respectively, as expected in a dinuclear complex where the hydride is trans to two of four phosphorus nuclei and cis to the other two, respectively. This assignment is based on the observation that J(P–H(trans)) is greater than J(P–H(cis)) in square-planar complexes. The magnitude of ^1J(Pt–H) is very low, consistent with values observed in other complexes containing bridging hydrogen.[2,4] The $^{31}P\{^1H\}$ spectrum at 303 K consists of a single signal at 16.6 ppm in CD_2Cl_2, ^1J(Pt–P) = 3660 Hz. At 213 K a complex pattern of two main resonances is observed: 21.5

Scheme I



ppm, ^1J(Pt–P) = 4690 Hz; 10.6 ppm, ^1J(Pt–P) = 2555 Hz. The large difference in the Pt–P coupling constants seems to reflect the difference in trans influence between the hydrido and the carbonyl ligand.

The isocyanide derivatives **4a** and **5a** are less stable in solution than the carbonyl complexes, and in no case was a well-resolved magnetic resonance spectrum obtained. For **5a**, however, both the ^{1}H and ^{31}P NMR gave evidence of nonfluxional behavior at 303 K: ^{1}H NMR τ 10 (triplet of triplets with satellites, ^1J(Pt–H) = ca. 490, ^2J(P–H) = ca. 80 and 10 Hz); ^{31}P NMR 42.03 (^1J(Pt–P) = 4560 Hz), 43.85 ppm (^1J(Pt–P) = 2290 Hz).

Finally, the ^{1}H NMR spectrum of **6a** in CD_3COCD_3 at 205 K shows a doublet of broad signals centered at τ 11.4 (^1J(Pt–H) = 985 Hz, ^2J(P–H(trans)) = 173 Hz; coupling to the cis phosphorus atom is not resolved). The large value of the Pt–H coupling constant is consistent with the presence of a terminal hydride, as suggested by the IR data.

Discussion of Valency and Mechanistic Aspects from the Point of View of the Syntheses and Spectra

The displacement of dihydrogen by carbon monoxide or isocyanides from the cationic dinuclear platinum trihydrides presents interesting valency and mechanistic problems. The product cations bear a formal relationship to the trimeric species obtained in the displacement of H_2 by CO in L_2PtH_2 complexes[11-13] but, by contrast, display low stretching frequencies for the bridging CO (or isocyanide) groups. This prompted us to engage in a structure study of one of these complexes. Crystals of **1a** were found to be suitable, and its structure determination is presented in the Experimental Section. Elimination of H_2 from the dinuclear trihydride complexes is a further example of the displacement of H_2 from polyhydrido metal cluster complexes,[14] processes that may be fundamentally related to the desorption of H_2 from the surface of metals or intermetallic solids.[15] Specifically related to the present work is the displacement of H_2 by CO or phosphines in the dinuclear cation $[PtH(\mu\text{-}H)(\mu\text{-dpm})_2PtH]^+$, dpm = bis(diphenylphosphino)methane,[16] or the reductive elimination of H_2 from $[IrH(CO)(\mu\text{-}S)(\mu\text{-dpm})_2IrH(CO)]$,[17a] "A-frame"[17b] complexes in which bidentate ligands are found bridging the two metal atoms. More recently, elimination of H_2 from dinuclear complexes has been demonstrated photochemically.[18] In some cases the displacement or elimination is reversible under ambient conditions. By contrast, the displacement observed in the present study is not.

The mechanistic problem has been succinctly stated by Geoffroy and co-workers,[18] namely, that elimination of dihydrogen is recognized as as an elementary process when the two hydrogen atoms are bonded to a single metal center.[9,11,12,19-23] Very little consideration has as yet been given to multicenter elimination as in polynuclear metal complexes.[24] We are thus led to postulate that the elimination of dihydrogen from the trihydrides occurs in a structural tautomer in which both hydrogen atoms to be eliminated are attached to a single metal center, shown as A^+ in Scheme I.

Such a tautomer has already been postulated to account for the fluxional behavior observed for hydrogen in these complexes.[4] It may be significant in this connection that the isocyanides give H_2 displacement reactions analogous to those of CO and not insertion products such as those containing the Pt—C(H)=NR group as reported in the studies of Christian and Clark.[25]

The first product of the displacement of H_2 proposed in Scheme I would be B^+ or C^+. Structure B^+ (with isocyanide in place of CO) is assigned to **6**$^+$, and we thus propose that this complex lies along the reaction coordinate, arrested from proceeding to the bridged structure D^+ perhaps for steric reasons. Cation **6**$^+$ is also obtained by displacement of CO from **1**$^+$ (structure D^+). Since the addition (or loss) of CO is not conceived directly from a bridging position, this transformation could occur through tautomer B^+ or C^+.

Structure D^+ proposed for the other derivatives isolated in this work and the one observed for **1**$^+$ (see structure determination described below) is dynamic. To account for the

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Table II. Crystal and Intensity Collection Data for $[Pt_2(\mu\text{-}H,\mu\text{-}CO)(Ph_2P(CH_2)_2PPh_2)_2][BF_4]$ (**1a**)

formula	$Pt_2P_4C_{53}H_{49}OBF_4$
fw	1302.8
a/Å	13.477 (5)
b/Å	11.090 (4)
c/Å	15.976 (8)
β/deg	97.40 (3)
V/Å^3	2368(2)
Z	2
ρ(calcd)/g cm^{-3}	1.83
space group	$P2/n$
cryst size/mm	0.2, 0.2, 0.1
temp/K	115
radiat source; λ/Å	Mo Kα (graphite monochromated); 0.710 69
abs coeff (μ)/cm^{-1}	61.5
transmissn factors	0.5666 (min)–0.7226 (max)
scan rate/deg min^{-1}	6
scan range: above Kα_1	1.5
below Kα_2	1.5
bkgd time	=scan time
2θ limits/deg	50
no. of unique data ($I_O > 3\sigma(I_O)$)	2494
final no. of variables	275
R/%[a]	3.5
R_w/%[b]	4.4

[a] $R = \Sigma||F_O| - |F_c||/\Sigma|F_O|$. [b] $R_w = [\Sigma w(|F_O| - |F_c|)^2/\Sigma w F_O{}^2]^{1/2}$, $w = 1/(\sigma^2|F_O|)$.

Table III. Positional Parameters for **1a**[a]

atom	x	y	z
Pt(1)	0.22655 (3)	0.11029 (4)	0.33016 (3)
C	0.2500	0.2449 (17)	0.2500
O	0.2500	0.3510 (10)	0.2500
P(1)	0.2063 (2)	−0.0647 (3)	0.4058 (2)
P(2)	0.1756 (2)	0.2127 (3)	0.4396 (2)
C(101)	0.1410 (8)	−0.1933 (9)	0.3549 (7)
C(102)	0.0437 (9)	−0.1766 (10)	0.3157 (8)
C(103)	−0.0104 (9)	−0.2722 (12)	0.2777 (8)
C(104)	0.0334 (10)	−0.3855 (12)	0.2783 (8)
C(105)	0.1302 (10)	−0.4023 (10)	0.3153 (9)
C(106)	0.1820 (9)	−0.3067 (12)	0.3528 (8)
C(111)	0.3231 (9)	−0.1183 (10)	0.4601 (7)
C(112)	0.4019 (10)	−0.1393 (10)	0.4125 (9)
C(113)	0.4963 (10)	−0.1680 (12)	0.4530 (10)
C(114)	0.5139 (9)	−0.1742 (12)	0.5401 (10)
C(115)	0.4375 (10)	−0.1512 (12)	0.5865 (8)
C(116)	0.3427 (9)	−0.1245 (10)	0.5468 (8)
C(201)	0.2491 (8)	0.3314 (10)	0.4952 (7)
C(202)	0.3037 (9)	0.4107 (10)	0.4489 (8)
C(203)	0.3647 (9)	0.4996 (10)	0.4910 (9)
C(204)	0.3698 (10)	0.5116 (11)	0.5766 (9)
C(205)	0.3180 (9)	0.4334 (11)	0.6223 (8)
C(206)	0.2564 (9)	0.3451 (11)	0.5807 (8)
C(211)	0.0487 (8)	0.2701 (9)	0.4112 (7)
C(212)	−0.0032 (11)	0.2386 (13)	0.3337 (7)
C(213)	−0.1022 (9)	0.2688 (11)	0.3125 (7)
C(214)	−0.1489 (9)	0.3357 (12)	0.3683 (8)
C(215)	−0.0995 (10)	0.3717 (10)	0.4438 (8)
C(216)	0.0003 (9)	0.3370 (10)	0.4661 (7)
C(2)	0.1634 (8)	0.1024 (10)	0.5244 (6)
C(1)	0.1262 (8)	−0.0206 (10)	0.4855 (6)
H	0.25	0.043 (7)	0.25
B	0.73685	0.94722	0.25994
	0.76315		0.24006
F(1)	0.75707	0.83077	0.22929
	0.74293		0.27071
F(2)	0.66630	0.93774	0.31835
	0.83370		0.18165
F(3)	0.69725	1.02180	0.19146
	0.80275		0.30854
F(4)	0.82652	0.99856	0.30088
	0.67348		0.19912

[a] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. The BF_4^- anion was treated as a rigid group found to be disordered about a twofold symmetry axis; see text. The six group coordinates (cf.: Sheringer, C. *Acta Crystallogr.* 1963, *16*, 546) are as follows. Fractional coordinates: $x = 0.6663$ (8); $y = 0.9377$ (9); $z = 0.3184$ (7). Angles: $\varphi = 0.2542$ (77) radians; $\theta = -2.7926$ (66) radians; $\rho = -0.6524$ (68) radians.

averaging process observed in the NMR, we propose that D^+ is involved in exchange with structure C^+, containing a hydrogen-bridged metal–metal bond. Rotation around this bond (or dissociation into two fragments and recombination) would equilibrate the phosphorus atoms.

Experimental Section

The starting platinum complexes $[Pt_2H_3(L\text{-}L)_2][A]$ were prepared as previously described for L-L = dpe, A = BF_4 or I.[2] Ligands dpp and dpb were obtained from Strem Chemicals. Isocyanides were prepared according to literature methods.[26] The reactions with isocyanides were initially carried out under a dinitrogen atmosphere; however, this precaution was found to be unnecessary and may be omitted.

Analyses were performed by the microanalytical laboratory of the University of Milan and by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, West Germany. Spectra were obtained as follows: IR, Beckman 4210 spectrophotometer; ^1H NMR, Varian XL 100; $^{31}P\{^1H\}$, Bruker WP 80 (32.4 MHz). ^{31}P chemical shifts are reported in parts per million relative to external 85% H_3PO_4, *upfield* being *negative*. Physical properties and analytical data for the new compounds are summarized in Table I.

Preparation of Carbonyl Derivatives 1–3. Initially the complexes were prepared in chloroform, dichloromethane, and acetone solutions in order to establish whether the solvent had any influence. The last is the solvent of choice, minimizing the formation of a yellow unidentified byproduct observed in the first two solvents. In a typical experiment, CO is bubbled at room temperature through a pale yellow solution of $[Pt_2H_3(dpe)_2][BF_4]$ (0.5 g) in acetone (40 mL); the solution turns dark in a few minutes. After 15 min under CO, the solution is eluted through a 20 × 1 cm column of deactivated alumina (10% H_2O). An analytically pure, turquoise-green complex is obtained by addition of methanol and concentration under water pump vacuum; yield of **1a** ca. 90%. Complexes **2a** (violet) and **3a** (pink-violet) are similarly prepared from $[Pt_2H_3(dpp)_2][BF_4]$ and $[Pt_2H_3(dpb)_2][BF_4]$, respectively. To isolate analytically pure **3a**, two crystallizations are required from acetone/ethyl ether after chromatography on Al_2O_3. Workup of the crude product yields a very small amount of a maroon hydrido complex (^1H NMR multiplet centered at τ 14.8), still under investigation. The corresponding iodide complex was obtained either by exchange reaction with KI in methanol suspension, followed by crystallization from dichloromethane/diethyl ether, or by bubbling CO directly in a chloroform solution of the corresponding iodo complexes of the dinuclear trihydrides. The deuterated complex **1a**-d_1 is prepared from the corresponding deuterated starting material $[Pt_2D_3(dpe)_2][BF_4]$.

Complex **1a** can also be obtained by reaction of CO directly with crystals of $[Pt_2H_3(dpe)_2][BF_4]$ at 341 K, these turning dark brown upon exposure to the gas. After ca. 100 h, workup gives **1a** in small quantities.

Preparation of Isocyanide Derivatives 4–6. (a) From the Trihydrides. The reactions are carried out in chlorinated solvents or in acetone. A 1:2 isocyanide:platinum ratio is required, and in all cases, the presence of excess ligand must be avoided. Typically, 0.3 mmol of the trihydrido complex is dissolved in 50 mL of acetone, and 0.32 mmol of isocyanide in 10 mL of acetone is added dropwise (ca. 15 min). The resulting dark solution is concentrated and, upon addition of diethyl ether, crude product obtained. To achieve analytically pure compounds, crystallization from acetone/diethyl ether or chromatography on deactivated Al_2O_3 is needed. Complex **6** is prepared in dichloromethane, precipitated with ether, and crystallized from acetone/ether. Yields, %: **4a**, 80; **4b**, 80; **5a**, 85; **5b**, 15; **6a**, 70. In the reaction between $[Pt_2H_3(dpe)_2][BF_4]$ and *p*-tolyl isocyanide, the amount of gas evolved was found to be 1.1 mol/mol of starting complex.

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(26) Ugi, I., Ed. "Isonitrile Chemistry"; Academic Press: New York, 1971.

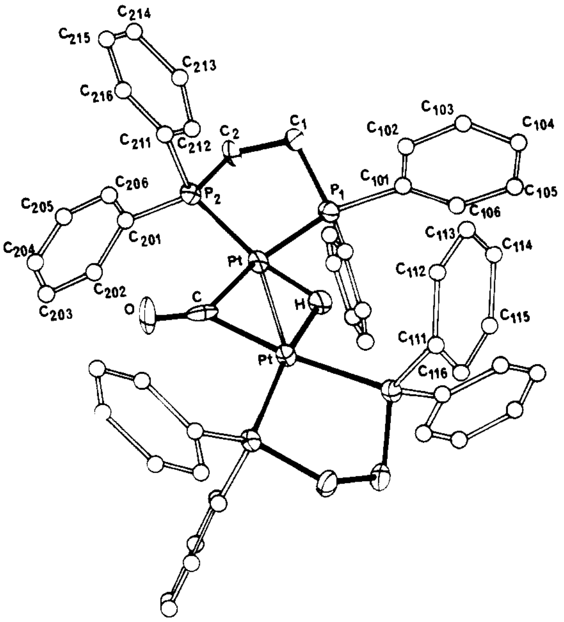

Figure 3. ORTEP diagram of 1^+, showing the numbering scheme. For the sake of clarity, the carbon atoms of the phenyl groups are depicted as small spheres of arbitrary diameter.

(b) From the Carbonyl Complexes. The displacement of CO by isocyanide was checked with three ligands, CH_3NC, p-$CH_3C_6H_4NC$, and $(CH_3)_3CNC$. In each case, displacement of CO was observed and complexes **4**, **5**, and **6** were obtained respectively, though with lower yields than in procedure a. In a typical experiment, 0.5 mmol of **1a** is dissolved in 50 mL of dichloromethane and treated with 0.52 mmol of p-$CH_3C_6H_4NC$ in the same solvent. The resulting dark red solution is concentrated to a small volume and eluted through a 20 × 1 cm column of deactivated Al_2O_3 (10% H_2O). From the first fraction (violet), a crude product is obtained by precipitation with diethyl ether; this is crystallized from acetone/diethyl ether to give **5a** in 60% yield. Complexes **4a** and **6** are obtained in the same way (50 and 27% yields, respectively). Complex **4b** is correspondingly obtained from **1b** (0.3 g) in acetone (50 mL); the solution is concentrated to 5 mL and the pink precipitate collected and crystallized from dichloromethane/diethyl ether (yield 8%).

X-ray Diffraction Studies of $[Pt_2(\mu\text{-}H,\mu\text{-}CO)(dpe)_2][BF_4]$ (1a). Collection and Reduction of the Data. A blue-green crystal of nearly cubic dimensions, suitable for X-ray diffraction studies, was obtained by slow evaporation of a ca. 1:1 CH_2Cl_2/CH_3OH solution of **1a**. This crystal was attached to a glass fiber and mounted on a Syntex $P\bar{1}$ automated diffractometer. Crystallographic data were obtained at 115 K with a device constructed by Dr. C. E. Strouse of this department.[27] Fifteen high-angle reflections were used as input to the automatic centering, autoindexing, and least-squares routines of the instrument and a set of lattice parameters was obtained; crystal data and parameters for collection of intensity data are given in Table II. The total background count time was equal to the scan time. Intensities for three standard reflections, (200), (221), and (210), were monitored after every 100 reflections; no significant changes were observed. A total of 7344 intensities were recorded, and 2494 reflections were used in the structural refinement.[28] These were considered observed, satisfying the requirement $I > 3\sigma(I)$. Systematic absences characteristic of the space group $P2/n$ were observed.[29] This space group requires that the molecule lie on a crystallographic twofold axis.

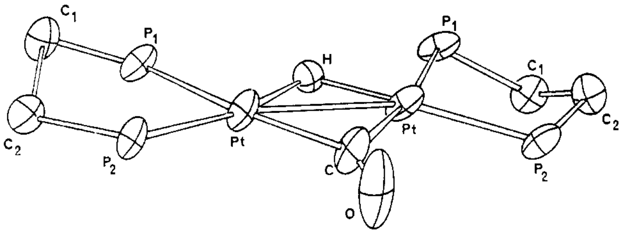

Figure 4. ORTEP diagram of 1^+, depicting the immediate coordination sphere around the platinum atoms. Principal distances and angles (see Table IV for esd's): Pt–Pt 2.716, Pt–H 1.55, Pt–C(O) 2.01 Å; Pt–H–Pt 122, Pt–C(O)–Pt 84.6°.

Table IV. Interatomic Distances (Å) for $[Pt_2(\mu\text{-}H,\mu\text{-}CO)(dpe)_2][BF_4]$ (1a)

Pt–Pt	2.716 (1)	C(201)–C(206)	1.37 (2)
Pt–C	2.01 (1)	C(201)–C(202)	1.42 (2)
Pt–P(2)	2.264 (3)	C(202)–C(203)	1.40 (2)
Pt–P(1)	2.321 (3)	C(203)–C(204)	1.37 (2)
Pt–H	1.55 (4)	C(204)–C(205)	1.38 (2)
C–O	1.17 (2)	C(205)–C(206)	1.40 (2)
P(1)–C(111)	1.80 (1)	C(211)–C(216)	1.38 (1)
P(1)–C(101)	1.81 (1)	C(211)–C(212)	1.39 (2)
P(1)–C(1)	1.84 (1)	C(212)–C(213)	1.38 (2)
P(2)–C(201)	1.81 (1)	C(213)–C(214)	1.37 (2)
P(2)–C(211)	1.83 (1)	C(111)–C(116)	1.38 (2)
P(2)–C(2)	1.85 (1)	C(111)–C(112)	1.40 (2)
C(1)–C(2)	1.55 (1)	C(112)–C(113)	1.39 (2)
C(101)–C(106)	1.38 (1)	C(113)–C(114)	1.38 (2)
C(101)–C(102)	1.39 (1)	C(114)–C(115)	1.37 (2)
C(102)–C(103)	1.38 (2)	C(115)–C(116)	1.38 (2)
C(103)–C(104)	1.39 (1)	C(214)–C(215)	1.36 (2)
C(104)–C(105)	1.37 (2)	C(215)–C(216)	1.40 (2)
C(105)–C(106)	1.38 (2)		

Solution and Refinement of the Structure. The atomic coordinates for the platinum atom were obtained from a Patterson map. A Fourier summation based on the platinum atom position revealed the positions of the two phosphorus atoms and several of the phenyl carbon atoms. Further refinement and difference Fourier syntheses led to the location of the remaining carbon atoms. The carbonyl carbon and oxygen were located on the C_2 axis, and their x and z coordinates were held constant for all refinements. The BF_4^- anion was found to be disordered and therefore was treated as a rigid group restricted to its known geometry, T_d symmetry, $d(B\text{–}F) = 1.43$ Å. The disorder was found to consist of two interpenetrating tetrahedra related by a twofold symmetry axis. Positional parameters showing partial occupancy for the atoms of this anion are given in Table III.

Refinement was carried out by use of full-matrix least-squares procedures.[28] The quantity minimized was $\sum w(|F_o| - |F_c|)$, where $w = 1/(\sigma^2|F_o|)$ and F_o and F_c are the observed and calculated structure amplitudes, respectively. The agreement indices for the refinement are given in Table II. After several cycles of least-squares refinement with the platinum and phosphorus assigned anisotropic thermal parameters, the discrepancy factors were $R = 0.133$ and $R_w = 0.172$. The data were then corrected for the effects of absorption ($\mu = 61.5$ cm^{-2}, maximum and minimum transmission factors being 0.5666 and 0.7226, respectively). A cycle of least-squares refinement gave $R = 0.078$ and $R_w = 0.091$, indicating the validity of the correction. Several more cycles of least-squares refinement including anomalous dispersion and anisotropic temperature factors for all atoms converged at $R = 0.043$ and $R_w = 0.05$.

Careful examination of the difference map at that point revealed the position of several of the phenyl hydrogens. The coordinates of the remaining hydrogen atoms were calculated at geometrically reasonable positions and were not refined. These are given in Table A (supplementary material). Inspection of the difference Fourier map along the crystallographically imposed C_2 axis revealed electron density in a position close to a calculated position of the bridging hydrogen. Other residual electron densities were located very close to the platinum but not along the C_2 axis; several were too close to the platinum atom(s) to be chemically meaningful.

Several more least-squares cycles with the hydrogen, allowed to refine in the y direction only, led to a final $R = 0.041$ and $R_w = 0.047$. The other hydrogen atoms were included in the structure factor

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(27) Strouse, C. E. *Rev. Sci. Instrum.* **1976**, *47*, 871.

(28) Programs used in this work: data reduction program PIBAR for the Syntex diffractometer (Bell and Murphy); JBPATT, JBFOUR, and PKLIST, modified versions of ORFLS and ORFFE (Busing, Martin, and Levy) for full-matrix least-squares and error analysis; ORTEP (Johnson) for structural plots; PUBLIST (Hoel) for structure factor table listing. All calculations were performed on the IBM 360/91 and 3033, operated by the UCLA Campus Computing Network. Atomic scattering factors for the non-hydrogen atoms were taken from standard tables[29] and for the hydrogen from Stewart et al.[30]

(29) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. 4.

(30) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table V. Selected Interatomic Angles (deg) for $[Pt_2(\mu\text{-}H,\mu\text{-}CO)(dpe)_2][BF_4]$ (1a)

H-Pt-P(2)	173.8 (6)	O-C-Pt	137.7 (4)
H-Pt-P(1)	94.3 (26)	Pt-C-Pt	84.6 (2)
C-Pt-P(2)	101.9 (4)	C(211)-P(2)-C(201)	107.7 (5)
C-Pt-P(1)	171.0 (4)	C(211)-P(2)-C(2)	102.5 (5)
P(2)-Pt-P(1)	87.1 (1)	C(201)-P(2)-C(2)	102.5 (5)
C(111)-P(1)-C(101)	107.5 (5)	C(201)-P(2)-Pt	122.9 (4)
C(111)-P(1)-C(1)	108.0 (5)	C(211)-P(2)-Pt	110.5 (4)
C(101)-P(1)-C(1)	103.1 (5)	C(2)-P(2)-Pt	107.4 (4)
C(101)-P(1)-Pt	120.5 (4)	Pt-H-Pt	122 (2)
C(111)-P(1)-Pt	111.9 (4)	P(2)-C(2)-C(1)	110.0 (7)
C(1)-P(1)-Pt	104.9 (4)	P(1)-C(1)-C(2)	108.9 (7)

Table VI. Pt-Pt Distances in CO-, CNR-, or SO_2-Bridged Triangulated Polynuclear Derivatives of Platinum(0)

complex	d_{Pt-Pt}/Å	ref
$[Pt_4(\mu\text{-}CO)_4(PMe_2Ph)_4]$	2.790 (7), 2.752 (7)	36a
$[Pt_3(\mu\text{-}CO)_3(CO)_3]_n{}^{2-}$ (n = 2, 3, 5)	2.66 ± 1[a]	36b
$[Pt_3(\mu\text{-}CN\text{-}t\text{-}Bu)_3(CN\text{-}t\text{-}Bu)_3]$	2.632[b]	37
$[Ru(L)(CO)_2(\mu\text{-}CO\text{-}PtL)_2(\mu\text{-}CO)]$ (L = PMe_2Ph)	2.647 (2)	38
$[PtL_2(\mu\text{-}CO\text{-}PtL)_2(\mu\text{-}CO)]$ (L = PPh_3)	2.675 (1), 2.736 (1), 2.714 (1)	11a
$[Pt_3(\mu\text{-}CO)_3(P(C_6H_{11})_3)_3]$	2.656 (2), 2.653 (2)	11b
$[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$	2.712 (1), 2.695 (1)	39

[a] Average of Pt-C_μ-Pt separations in all of the ions. [b] Average of three Pt-C_μ-Pt separations.

calculations, but their parameters were not varied.

During these final refinements with all non-hydrogen atoms allowed to vibrate anisotropically, one of the carbon atoms became nonpositive definite and was therefore constrained to vibrate isotropically for the remaining least-squares cycles.

The final atomic positions are given in Table III together with their estimated standard deviations based on the final least-squares correlation matrix, including the errors in the unit cell parameters. Thermal parameters and observed and calculated structure factor amplitudes are given in Tables B and C, respectively (supplementary material).

Description and Discussion of the Structure of 1a

Crystals of **1a** are monoclinic and contain two $[Pt_2(\mu\text{-}H,\mu\text{-}CO)(dpe)_2]^+$ cations and two BF_4^- anions per unit cell. The anions are well separated; the closest contact between nonhydrogen atoms is between cation and anion, C(2)···F = 2.986 Å. The closest contact between cations is C(205)···C(214) = 3.444 Å. There are no interanionic contacts below 3.6 Å. The cation consists of a discrete dinuclear unit shown in Figure 3 along with its numbering scheme. A view of the dinuclear unit showing only the atoms within the coordination sphere of the platinum atoms is shown in Figure 4. Interatomic distances and angles are given in Tables IV and V, respectively. Some nonbonding distances are also listed in Table IV.

The cation contains two platinum atoms with a distorted square-planar configuration about each of the metals. Two phosphorus atoms cis to one another, the carbon atom of the bridging carbonyl group, and the bridging hydrogen are located at the corners of the square. The bridging hydrogen atom and carbonyl group lie on the C_2 axis bisecting the Pt-Pt vector. The bidentate phosphine ligands form an angle of 87.1 (1)° with the platinum atom; other angles in the coordination sphere are C_μ-Pt-P(2) = 101.9 (4)° and H_μ-Pt-P(1) = 94 (2)°. There is a slight distortion of the diphosphine group away from the bridging carbonyl, toward the less sterically demanding bridging hydrogen atom. Distortions of up to 7-10° from idealized geometry have been observed[9,31,32] and may be expected from a theoretical point of view[33] in coordination situations involving hydrogen. The phosphorus-platinum distances are 2.264 (3) Å (trans to the bridging hydrogen) and 2.321 (3) Å (trans to the carbonyl carbon). These are similar to other reported phosphorus-platinum distances, which have been summarized elsewhere.[4] A slight lengthening is observed in the Pt-P separation trans to the carbonyl group and may be understood to derive from a trans influence of such a group being apparently larger than from the hydrogen, both in bridging position. The low trans influence of the bridging hydride has been previously noted.[34]

The Pt-Pt distance of 2.716 (1) Å is close to what has been observed in other complexes considered to contain Pt(0)-Pt(0) separations.[13,35] The first observation of an *unbridged* Pt(0)-Pt(0) separation is that of Ibers and Otsuka[35a] in the dimer $[Pt(L\text{-}L)]_2$, L-L = $(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2$, in which the Pt-Pt distance is observed to be 2.765 (1) Å. Pt-Pt separations in several bridged polynuclear Pt(0) complexes are given in Table VI.[11,12,36-39] There is some drift in these data to lower values overlapping the upper end of what is called the characteristic Pt(I)-Pt(I) separation.[13] We believe that overlap in these ranges is inevitable, given the uncertainties associated with the "expected" value.[35b] The relatively narrow range observed for the data in Table VI may well be a result of the presence of the bridging groups.

Another interesting point regarding the dinuclear cation is the very low position for the stretching absorption of the carbonyl bridging group. This parallels observations of similar low bridging absorptions in a number of "A-frame" complexes,[40-46] summarized in Table VII, as well as in the complex $[Mn(dppe)(CO)_2(\eta^1,\eta^2{:}\mu\text{-}CO)Mn(dppe)(CO)_2]$.[47] In the latter the absorption of the bridging CO is observed at 1650 cm^{-1}. For a time it was believed that all bridging carbonyl groups exhibiting an anomalously low stretching absorption existed in the $\eta^1,\eta^2{:}\mu$-coordination. In the "A-frame" complexes exhibiting the anomalously low bridging carbonyl absorption, the bridging CO group takes its usual μ-C(O) pos-

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(35) (a) Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063. (b) In valence bond terms, the single-bond order observed in the separation of two Pt(0) centers is understood as a resonance hybrid containing equal amounts of a "no-bond" d^{10}-d^{10} canonical structure and a "double-bonded" d^9s^1-d^9s^1 promoted form. This is equivalent to invoking configuration interaction in the molecular orbital treatment[13] between the totally filled bonding and antibonding levels arising from the d orbitals and the totally empty bonding and antibonding combinations arising from the metal s orbitals. Various admixtures of the valence-bond canonical extremes (or varying degrees of configuration interaction in the molecular orbital language) could thus lead to a wide variation in bond order from 0 (in one extreme) to 2 (in the other extreme) in these Pt(0)-Pt(0) dimers. This would be reflected in a wide variation of Pt-Pt separations except perhaps where accompanied by bridging groups such as the CO group; see Table VII.

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Table VII. Comparison of ν(CO) (or ν(C=NR)) and Structural Parameters in CO- (or C=NR-) Bridged "A-Frame" Complexes[a] with Those in **1a**

complex	$\nu(\mu\text{-CO})/\text{cm}^{-1}$	$d_{\text{M-M}}/\text{Å}$	M-C_μ-M/deg	ref
$[Pd_2(\mu\text{-dpm})_2(\mu\text{-CO})Cl_2]$	1704			40
$[Pd_2(\mu\text{-dpm})_2(\mu\text{-C=NCH}_3)(CNCH_3)_2]^{2+}$ [b]	(1640-1680)[c]	3.215 (2)	106 (1)	40
$[Pt_2(\mu\text{-dpm})_2(\mu\text{-CO})Cl_2]$	1638			42a
$[Pd_2(\mu\text{-dam})_2(\mu\text{-CO})Cl_2]$	1720	3.274 (8)	119 (3)	41
$[Pt_2(\mu\text{-dam})_2(\mu\text{-CO})Cl_2]$	1635	3.162 (4)	106 (3)	42b
$[Ir_2(\mu\text{-S},\mu\text{-CO})(\mu\text{-dpm})_2(CO)_2]$	1760	2.843 (2)	86.7 (6)	17
$[Rh_2(\mu\text{-Cl},\mu\text{-CO})(\mu\text{-dpm})_2(CO)_2]^+$				
BPh_4^- salt	1863	2.8415 (7)	86.7 (3)	43
$RhCl_2(CO)_2^-$ salt	1865	2.838 (1)	86.4 (1)	44
$[Pt_2(\mu\text{-H},\mu\text{-CO})(dpe)_2][BF_4]$ (**1a**)	1720	2.716 (1)	84.6 (2)	this work

[a] dpm = bis(diphenylphosphino)methane; dam = bis(diphenylarsino)methane. [b] As the PF_6^- salt. [c] $\nu(\mu\text{-C=NR})$.

ition, as is also seen in **1**$^+$. A significant variation, however, is seen in the M-C_μ-M angle, which correlates with the M-M separation as indicated in Table VII. The long metal-metal separations of ca. 3.1-3.3 Å involve very little metal-metal bonding[46] and are associated with a wide M-C_μ-M angle, ca. 120°. This is close to that in organic carbonyl compounds, which has led to assignment of the bridging carbonyl group in these complexes as a doubly negatively charged species, i.e. a "demetalated" formaldehyde.[45,46] This requires an increase of the formal oxidation state of the metal by 1 unit: for instance, the complexes thus bridged (Table VII) are regarded as Pt(II)-Pt(II) dimers. Clearly this is *not* the case in the present structure where the Pt-C_μ-Pt angle is 84.6 (2)°, close to that in derivatives where the bridged CO group is taken to be a *two*-electron donor.[46] The structural data thus indicate assignment of these carbonyl- (or isocyanide-) bridged dinuclear cations as protonated Pt(0) dimers. The unusually low stretching absorption for the bridging group is anomalous compared to that in the derivatives listed in Table VI; in these the bridging absorptions occur in the higher range (near 1800 cm^{-1}). This difference is most likely derived from the high degree of electron-releasing ability of the chelating diphosphines in the present dinuclear cations.

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Registry No. **1a**, 72269-74-0; **1a**-d_1, 86162-52-9; **1b**, 72269-75-1; **2a**, 86162-42-7; **3a**, 86162-43-8; **4a**, 72166-98-4; **4b**, 72166-99-5; **5a**, 72339-25-4; **5a**-d_1, 86162-54-1; **5b**, 72166-96-2; **6a**, 86162-45-0; **6a**-d_1, 86176-86-5; $[Pt_2H_3(dpe)_2][BF_4]$, 86176-88-7; $[Pt_2H_3(dpp)_2][BF_4]$, 86162-47-2; $[Pt_2H_3(dpb)_2][BF_4]$, 86162-49-4; $[Pt_2H_3(dpe)_2][I]$, 86162-50-7; Pt, 7440-06-4; deuterium, 7782-39-0.

Supplementary Material Available: Tables A-C, listing hydrogen atom coordinates, thermal parameters, and calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

Notes

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Pulse Radiolysis Studies of Californium(III) in Aqueous Perchlorate Solution. Evidence for the Preparation of Californium(II)[1]

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The solution chemistry of the transplutonium elements Am, Cm, Bk, and Cf has been limited primarily to the reactions of these elements in the +3 oxidation state.[2] Quasi-thermodynamic arguments have been advanced to predict that the +2 and +4 oxidation states of these elements are respectively powerful reductants and oxidants.[3] We have previously demonstrated that the divalent and tetravalent oxidation states of Am and Cm can be prepared as transient species[4] in aqueous noncomplexing media with the hydrated electron as reductant and the OH radical as oxidant. In this report we present evidence for the production of the hitherto undescribed aqueous oxidation state Cf(II) and the results of attempts to prepare Cf(IV) by pulse radiolysis techniques.

Experimental Section

Sodium hydroxide, perchloric acid, and *tert*-butyl alcohol stock solutions were prepared from analytical grade reagents and standardized by conventional techniques. The ^{249}Cf ($t_{1/2}$ = 350 years) was obtained as the product of the β^- decay of several milligrams of ^{249}Bk ($t_{1/2}$ = 314 days), which had been produced by Oak Ridge National Laboratory. The ^{249}Cf was purified by a series of ion-exchange procedures previously detailed,[5] followed by evaporation to dryness and precipitation of the hydroxide (immediately prior to the pulse irradiation), which was then washed and finally dissolved in the minimum amount of perchloric acid. This procedure was adopted to minimize introduction of impurities by the self-radiolysis of the solutions of the ^{249}Cf (9×10^6 disintegrations $\text{min}^{-1}\ \mu\text{g}^{-1}$). The Cf concentrations in the stock solutions were determined by α assays of aliquots with a 51% geometry α proportional counter.

After the pH was adjusted to 5.1-5.3 with NaOH solution, the Cf(III) solutions (5.5×10^{-4} M) were introduced into the gas-satu-

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