Synthesis, X-ray Structural Analysis, and Thermal Decomposition of the Platinum(II) Carboxylic Acid (Hydroxycarbonyl) *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$. Formation of a Diplatinum(II) Complex Containing Carbon Dioxide

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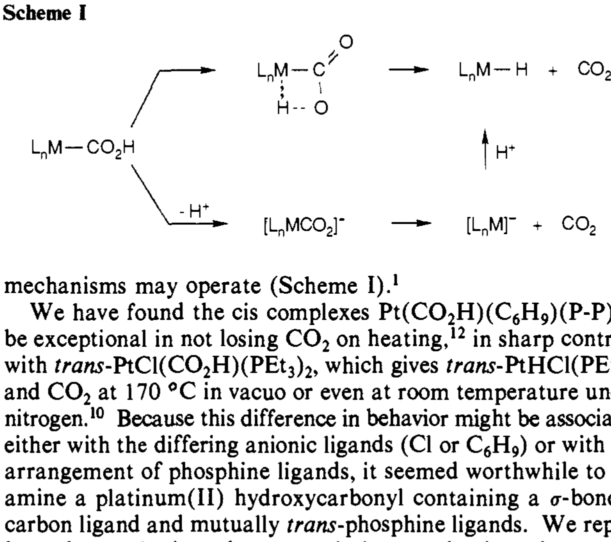
Abstract: Carbon monoxide reacts at atmospheric pressure and temperature with *trans*-$Pt(OH)(C_6H_5)(PEt_3)_2$ (**1**) to give a metallacarboxylic acid, *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (**2**). Crystals of **2** are monoclinic, space group $C2/c$, $a = 15.006$ (2) Å, $b = 11.520$ (2) Å, $c = 27.135$ (6) Å, $\beta = 89.90$ (1)°, $Z = 8$, at 175 K. The structure was solved by heavy atom methods and refined by least-squares techniques to $R = 0.033$ ($R_w = 0.038$) for 3070 unique data ($I > 3\sigma(I)$). It consists of a dimer in which two planar *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ units are joined by hydrogen bonding between the carboxylate groups. This structure, the O–H···O distance of 2.695 Å, and the metrical data for the carboxylate group [r(C=O) = 1.238 (11) Å, r(C–O) = 1.334 (10) Å, and O–Ĉ–O = 117.7 (8) Å] are similar to those found for many organic carboxylic acids. Solutions of **2** in organic solvents contain monomer and dimer in equilibrium; in formamide and *N*-methylformamide, dissociation to $[Pt(C_6H_5)(CO)(PEt_3)_2]OH$ takes place. This dissociation accounts for many of the reactions of **2**, e.g., facile exchange in the CO_2H group with CO and reaction with HBF_4, HCl, CH_3OH, and $(CH_3)_2NH$ to give, respectively, $[Pt(C_6H_5)(CO)(PEt_3)_2]BF_4$, $[Pt(C_6H_5)(CO)(PEt_3)_2]Cl$, $Pt(CO_2Me)(C_6H_5)(PEt_3)_2$, (**3**), and $Pt(CONMe_2)(C_6H_5)(PEt_3)_2$ (**4**) (trans isomers in all cases). Although **2** does not form salts with KOH, $KHCO_3$, or tertiary amines, it does react reversibly with its precursor **1** in a kind of acid–base or esterification reaction to give a dinuclear platinum(II) complex containing a μ_2-CO_2 ligand, [*trans*-$Pt(C_6H_5)(PEt_3)_2]_2$ (μ_2-CO_2) (**5**), which has been identified by its NMR (^{13}C, ^{31}P, and ^{195}Pt) and IR spectra. Complex **5** is also formed, together with ca. 0.5 mol of CO, when **2** is heated at ca. 100 °C. This mode of decomposition contrasts with that normally observed for metallacarboxylic acids, viz. formation of a metal hydride and loss of CO_2.

Metallacarboxylic acids (metal hydroxycarbonyls), L_nMCO_2H, are believed to be important intermediates in various transition-metal-mediated reactions of CO and water,[1] but only recently have compounds of this class been isolated and characterized. They include (η^5-C_5H_5)$M(CO_2H)(CO)(PPh_3)$, (M = Fe[2a,b],Ru[2b]), (η^5-C_5H_5)$Re(CO_2H)(CO)(NO)$,[3] (η^5-C_5H_5)$Re(CO_2H)(CO)(N_2Ar)$,[4] (η^5-C_5H_5)$Mo(CO_2H)(CO)_2(PPh_3)$,[5] $[Ru(CO_2H)(CO)(bipy)]^+$,[6] $IrCl_2(CO_2H)(CO)(PMe_2Ph)_2$,[7] $IrCl_2(CO_2H)(PMe_2Ph)_3$,[8] *trans*-$[IrH(CO_2H)(dppe)_2]^+$,[9] *trans*-$PtCl(CO_2H)(PEt_3)_2$,[10] and *cis*-$Pt(CO_2H)R(P\text{-}P)$ [R = CH_3, CH_2CN, CF_3, 1-cyclohexenyl(C_6H_9); P-P = various bis(tertiary phosphines)].[11,12] Despite these efforts, little is known about the chemistry of metal hydroxycarbonyls, especially about the factors that affect their acidic and basic properties, and there is no structural information. Most hydroxycarbonyls decompose on warming to give carbon dioxide and either the metal hydride or its conjugate base. However, the conditions required for this decomposition are by no means uniform, and it is not known whether it proceeds by β-hydride transfer to the metal or by deprotonation to yield an intermediate CO_2 complex; both mechanisms may operate (Scheme I).[1]

Scheme I



We have found the cis complexes $Pt(CO_2H)(C_6H_9)(P\text{-}P)$ to be exceptional in not losing CO_2 on heating,[12] in sharp contrast with *trans*-$PtCl(CO_2H)(PEt_3)_2$, which gives *trans*-$PtHCl(PEt_3)_2$ and CO_2 at 170 °C in vacuo or even at room temperature under nitrogen.[10] Because this difference in behavior might be associated either with the differing anionic ligands (Cl or C_6H_9) or with the arrangement of phosphine ligands, it seemed worthwhile to examine a platinum(II) hydroxycarbonyl containing a σ-bonded carbon ligand and mutually *trans*-phosphine ligands. We report here the synthesis and structural characterization of *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ and show that it decomposes in an unexpected manner to give a dinuclear μ-carbon dioxide complex of platinum(II).

Experimental Section

Spectroscopic measurements, microanalyses, and molecular weight determinations were carried out as described in an earlier paper.[12] Starting materials were obtained from the commercial suppliers listed previously.[12] The complex *trans*-$Pt(OH)(C_6H_5)(PEt_3)_2$ (**1**) was prepared by a slight modification of the literature method.[13]

Preparation of *trans*-Bis(triethylphosphine)(hydroxycarbonyl)(phenyl)platinum(II), *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (2). A solution of **1** (0.181 g, 0.344 mmol) in isopentane (3 mL) was stirred at slightly above atmospheric pressure of carbon monoxide for 10 min at room temperature. A white solid began to precipitate within 2 min. After the gas had been vented, the solvent was evaporated under reduced pressure until the volume of solution was ca. 1 mL. The initially colorless solution was now

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pale orange. The white solid was removed by centrifugation, washed with a few mL of cold isopentane, and dried in vacuo to give microcrystalline **2** (0.177 g, 0.320 mmol, 93%).

Anal. Calcd for $C_{19}H_{36}O_2P_2Pt$: C, 41.23; H, 6.56; P, 11.19; mol wt, 554. Found: C, 41.01; H, 6.61; P, 10.98; mol wt (osmometry, CH_2Cl_2) 518.

The ^{13}C-labeled analogue **2a** was prepared similarly by use of ^{13}CO enriched to 99%.

Diffraction quality crystals of **2** were formed as follows. A saturated solution of **1** in isopentane at −68 °C was allowed to warm to room temperature and stirred under CO for 10 min; no precipitate was observed. After several days at −18 °C, well-formed crystals of **2** were present.

The reaction of **1** with CO was studied by NMR spectroscopy as follows. A solution of **1** (0.120 g, 0.228 mmol) in toluene-d_8 (2.2 mL) was placed in a 10-mm NMR tube fitted with a septum cap which was secured with Teflon tape. The tube was cooled in a dry ice–ethanol bath, evacuated, and pressurized with ^{13}CO(150 kPa). Between −80 °C and −35 °C the only carbonyl-containing species detectable by ^{13}C NMR spectroscopy was dissolved ^{13}CO (δ184.3). Above −35 °C singlets at δ 205 and δ 200 due to **2a** and the μ_2-$^{13}CO_2$ complex **5a** (see below) appeared. At room temperature the only species present were **2a** and ^{13}CO, as shown by ^{13}C and ^{31}P NMR spectra.

Reactions of 2. (1) Fluoroboric Acid. A solution of **2a** (0.010 g, 0.018 mmol) in CD_2Cl_2 (0.5 mL) was treated with a solution of $HBF_4{\cdot}OEt_2$ (0.0023 mL, 0.018 mmol) in CD_2Cl_2, and the ^{13}C and ^{31}P NMR spectra were recorded in situ. The solution was evaporated to dryness under reduced pressure, and the IR spectrum of the resulting pale yellow solid was measured in a KBr disk. These measurements showed the product to be *trans*-$[Pt(C_6H_5)(^{13}CO)(PEt_3)_2]BF_4$: ^{13}C NMR (CD_2Cl_2) δ 178.6 (t with ^{195}Pt satellites, $^2J_{PC}$ = 8.8 Hz, $^1J_{PtC}$ = 947 Hz); ^{31}P NMR (CD_2Cl_2) δ 16.3 (d with ^{195}Pt satellites, $^2J_{PC}$ ca. 8 Hz, $^1J_{PtP}$ = 2315 Hz); IR (KBr) 2073 vs (C≡O) cm^{-1}.

(2) Hydrogen Chloride. A solution of **2a** (0.014 g, 0.025 mmol) in CD_2Cl_2 (2.2 mL) was transferred under nitrogen to a 10-mm NMR tube fitted with a septum cap. The tube was cooled in a dry ice–ethanol bath, and HCl (0.6 mL, ca. 0.025 mmol) was added slowly from a gas syringe. The tube was shaken to mix the contents, and ^{13}C and ^{31}P NMR spectra were measured at −80 °C. The main species present were *trans*-$[Pt(C_6H_5)(^{13}CO)(PEt_3)_2]Cl$, which had δ_C 177.7 ($^1J_{PtC}$ = 959 Hz) and δ_P 17.0 ($^1J_{PtP}$ = 2286 Hz, $^2J_{PC}$ = 8.3 Hz), and ^{13}CO (δ_C 183.7). There was also a small amount of *trans*-$PtCl(C_6H_5)(PEt_3)_2$ [δ_P 15.7, $^1J_{PtP}$ = 2754 Hz]. On warming to room temperature, the signals due to *trans*-$[Pt(C_6H_5)(CO)(PEt_3)_2]Cl$ disappeared, and only those due to ^{13}CO (δ_C 184.5) and *trans*-$PtCl(C_6H_5)(PEt_3)_2$ (δ_P 14.8, $^1J_{PtP}$ = 2795 Hz) remained.

(3) Hydrogen Sulfide. The reaction was studied as in (2). In CD_2Cl_2 at −80 °C the species present were ^{13}CO (δ_C 183.7) and *trans*-$Pt(SH)(C_6H_5)(PEt_3)_2$ (δ_P 10.5, $^1J_{PtP}$ = 2709 Hz). The same species were observed at room temperature, though the spectral parameters had changed slightly: ^{13}CO (δ_C 184.5) and *trans*-$Pt(SH)(C_6H_5)(PEt_3)_2$ (δ_P 10.4, $^1J_{PtP}$ = 2751 Hz).

(4) Methanol. A solution of **2a** (0.050 g, 0.090 mmol) in dry methanol (2 mL) was set aside at room temperature for 2 h and then evaporated to dryness under reduced pressure. The residual white solid was washed with isopentane and dried in vacuo to give *trans*-$Pt(^{13}CO_2Me)(C_6H_5)(PEt_3)_2$ (**3**) (0.039 g, 0.069 mmol, 76%): ^1H NMR (CD_2Cl_2) δ 3.43 (s with ^{195}Pt satellites, OMe, $^4J_{PtH}$ = 4 Hz); ^{13}C NMR (CD_2Cl_2) δ 203.1 (t with ^{195}Pt satellites, $^2J_{PC}$ = 11.6 Hz, $^1J_{PtC}$ = 853 Hz); ^{31}P NMR (CD_2Cl_2) δ 11.0 ($^2J_{PC}$ = 11.7 Hz, $^1J_{PtP}$ = 2779 Hz); IR (KBr) 1622 s (^{12}C=O), 1582 s (^{13}C=O) cm^{-1}. Anal. Calcd for $C_{20}H_{38}O_2P_2Pt$: C, 42.33; H, 6.75. Found: C, 41.99; H, 6.64.

(5) Dimethylamine. A stirred solution of **2a** (0.060 g, 0.108 mmol) in ether (7 mL) was treated with gaseous dimethylamine (5 mL, ca. 0.21 mmol) and stirred for 9 h at room temperature. Evaporation to dryness under reduced pressure gave an oily solid which was washed with isopentane and dried in vacuo. There was obtained *trans*-$Pt(^{13}CONMe_2)(C_6H_5)(PEt_3)_2$ (**4**) (0.047 g, 0.081 mmol, 75%) as a waxy, hygroscopic solid: ^1H NMR (CD_2Cl_2) δ 3.29 (d with ^{195}Pt satellites, NMe, $^3J_{CH}$ = 3.7 Hz, $^4J_{PtH}$ = 5.9 Hz, NMe), 2.69 (d, NMe, $^3J_{CH}$ = 2.2 Hz); ^{13}C NMR (CD_2Cl_2) δ 203.8 (t with ^{195}Pt satellites, $CONMe_2$, $^2J_{PC}$ = 10.3 Hz, $^1J_{PtC}$ = 756 Hz); ^{31}P NMR (CD_2Cl_2) δ 9.4 ($^2J_{PC}$ = 10 Hz, $^1J_{PtP}$ = 2858 Hz); IR (KBr) 1505 s (^{13}C=O) cm^{-1}. Anal. Calcd for $C_{21}H_{41}ONP_2Pt{\cdot}0.4H_2O$: C, 42.91; H, 7.17. Found: C, 42.98; H, 7.62.

(6) Carbon Monoxide. A solution of **2a** (0.010 g, 0.018 mmol) in THF (1.5 mL) was stirred under CO (14 kPa) at room temperature. Samples (ca. 0.3 mL) were withdrawn periodically, and their IR spectra were measured in KBr solution cells. Over a 1-h period the band due to ^{13}C=O stretching at 1553 cm^{-1} disappeared and was replaced by the corresponding ^{12}C=O band at 1592 cm^{-1}. There was also some decomposition induced by CO, as shown by new C≡O bands at 2040 cm^{-1} (m) and 1873 cm^{-1} (m br).

Thermal Decomposition of *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (2) or *trans*-$Pt(^{13}CO_2H)(C_6H_5)(PEt_3)_2$ (2a) in the Solid State. In a typical experiment, a sample tube containing **2** or **2a** (0.020 g, 0.036 mmol) was immersed in an oil bath which had been heated to a predetermined temperature in the range 60–100 °C. A stream of nitrogen was passed over the sample and then through Dräger indicator tubes for CO and CO_2. The sample was held at the given temperature for 1.5 h and allowed to cool to room temperature, and the ^{31}P NMR spectrum of the residue was recorded in C_6D_6 solution. Slow decomposition was observed at ca. 65 °C, but at 85 °C the complex $[Pt(C_6H_5)(PEt_3)_2]_2(\mu\text{-}CO_2)$ (**5**), or its ^{13}C-labeled analogue **5a**, was formed quantitatively as a waxy, orange solid, identified by ^{13}C and ^{31}P NMR spectroscopy (Table III). At this temperature the Dräger tubes showed an amount of CO corresponding approximately to a 1:2 mol ratio of CO to Pt as well as traces of CO_2. Extraction of the residue with isopentane and evaporation of the solvent under reduced pressure gave **5** in 90% yield.

Anal. Calcd for $C_{37}H_{70}O_2P_4Pt_2$: C, 41.88; H, 6.65; P, 11.68. Found: C, 41.78; H, 6.90; P, 10.37. At 90 °C or above, a second, as yet unidentified product was formed together with **5**: ^{13}P NMR (C_6D_6) δ 17.2 ($^1J_{PtP}$ = 2681 Hz).

Reaction of *trans*-$Pt(OH)(C_6H_5)(PEt_3)_2$ (1) with *trans*-$Pt(^{13}CO_2H)(C_6H_5)(PEt_3)_2$ (2a). A solution of **1** (ca. 0.1 g, 0.18 mmol) in toluene-d_8 or CD_2Cl_2 (1.7 mL) was added to an equimolar amount of solid **2a** at room temperature, and the mixture was stirred briefly. The NMR spectra (^1H, ^{13}C, ^{31}P, and ^{195}Pt) of the solution showed the main species present to be **5a**, but unreacted **1** and **2a** were also present. The ^1H NMR spectrum showed a broad singlet at ca. δ 5.7, which was not present in the spectra of starting materials or solvents and which is assigned to water. Solvent was allowed to evaporate from the mixture at atmospheric pressure, and the residue was redissolved in toluene-d_8 or CD_2Cl_2. The NMR spectra now showed a substantial increase in the concentration of **5a** and a marked decrease in the concentrations of **1** and **2a**.

Collection and Reduction of X-ray Data. Crystals of **2**, formed as described above, were all too large for direct use in data collection. However, crystals were easily cut parallel to the developed forms [{110},{001}], and diffraction quality fragments were obtained in this way. One fragment was used for collection of a partial room temperature data set which was subsequently discarded because of excessive crystal degradation (ca. 40% in 2.5 days). A second fragment was used for collection of the low-temperature data on which the present analysis is based. Both fragments were of similar size and were checked for quality photographically prior to diffractometry. That used in the present (low-temperature) analysis had approximate dimensions 0.125 × 0.150 × 0.175 mm parallel to the reciprocal lattice vectors 110, 110, and 001, respectively.

Low-temperature reflection intensities[14] were recorded on a Philips PW1100/20 diffractometer operating in θ–2θ scan mode [scan velocity 4° min^{-1} 2θ, 2 × 4 s backgrounds at extremes; Mo K$\bar{\alpha}$ radiation, graphite crystal monochromator; forms recorded $\pm h$+k+l, 4 < 2θ < 55°; 5807 reflections including standards (three every 60 min)]. Throughout the data collection the crystal temperature was maintained at 175 ± 2 K by means of a Leybold–Heraeus nitrogen cooling device. Additional experimental details are given in Table I together with the crystal data. Room temperature cell dimensions are from least-squares analysis of setting angles for 12 well-centered reflections [FACS-1 diffractometer, Mo Kα_1, 31 < 2θ < 40°] and low-temperature values from setting angles for 25 reflections [PW1100/20 diffractometer, Mo Kα_1, 35 < 2θ < 48°]. "Standards" intensities decreased by 9.7% (802), 5.6% (061), and 4.2% (0014), respectively, during the experiment, and data were corrected accordingly.[15] Data were also corrected for specimen absorption effects (SHELX),[16] but not for extinction, and were reduced to $|F_o|$ and $\sigma|F_o|$ values as described previously (ρ^2 = 0.002 assumed).[17,18] Sorting and averaging of equivalent forms yielded 3070 unique reflections with $I \geq 3\sigma(I)$. The value of $R_{int} = [\sum|F_o - \langle F_o\rangle|/\sum|F_o|]$ for 174 multiple observations was 0.030.

Solution and Refinement of the Structure. The structure was solved by conventional Patterson & Fourier techniques and refined by full-matrix least-squares analysis (SHELX)[16] minimizing $\sum w(|F_o| - |F_c|)^2$, with anisotropic thermal parameters specified for all non-hydrogen atoms.

(14) The room temperature data were recorded on a Picker FACS-1 diffractometer, also with graphite-monochromated Mo K$\bar{\alpha}$ radiation.

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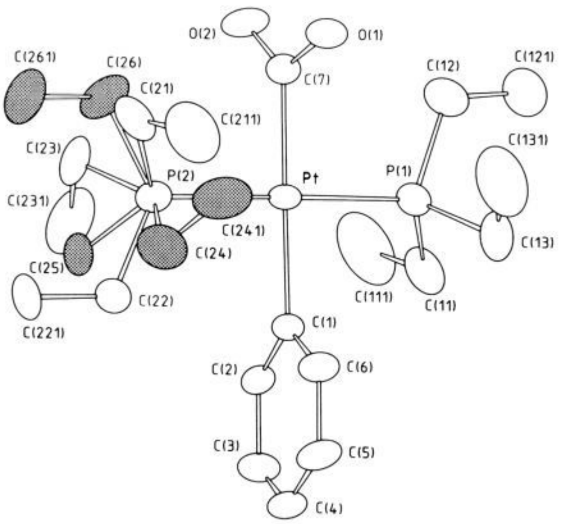

Figure 1. Atomic nomenclature for *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (**2**). Hatched atoms depict 38% occupancy sites in the disordered PEt_3 group; H-atoms omitted for clarity; 30% ellipsoids.

Table I. Crystal Data and X-ray Experimental Detail for *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (**2**)

M_r	553.5	
space group	$C2/c$	
Z	8	
a (Å)	15.079 (3)[a]	15.006 (2)[b]
b (Å)	11.590 (3)[a]	11.520 (2)[b]
c (Å)	27.322 (7)[a]	27.135 (6)[b]
β (deg)	90.25 (1)[a]	89.90 (1)[b]
V (Å^3)	4774.9[a]	4690.8[b]
temp (K)	294 ± 1	175 ± 2
ρ_{obsd} (g cm^{-3})	1.55 (1)	
ρ_{calcd}	1.54[b]	
μ (cm^{-1})	61.6	
λ (Å)	0.7107	
transmission range	0.404–0.531	
$2\theta_{max}$ (deg)	55	
unique reflcns	3070 [$I \geq 3\sigma(I)$]	
R	0.033	
R_w	0.038	

[a] Room-temperature cell. [b] Low-temperature cell.

Hydrogen atoms were located by calculation (C–H = 0.95 Å assumed), and group isotropic thermal parameters (one each for CH_2, CH_3, and aromatic hydrogens) were refined. The carboxylic hydrogen atom could not be located in difference maps and was not included in the scattering model. One of the two PEt_3 groups exhibits rotational disorder about the P–Pt bond. Refined occupancy factors for the ethyl groups of the preferred "rotamer" averaged 0.62 and, in the final refinement cycles, were fixed at that value.[19] Platinum atom scattering factors with anomalous dispersion corrections were taken from ref 20; for P, O, C, and H values supplied by SHELX[16] were employed. At convergence $R = 0.033$ and $R_w = 0.038$. Shift-to-error ratios were uniformly less than 0.2, and features in the final difference Fourier map did not exceed 0.7 eÅ^{-3} in magnitude. There was no evidence of significant extinction or of serious weighting anomalies. Final atomic coordinates together with estimated standard deviations are listed in Table II, and bond lengths and interbond angles are in Table III. The atomic nomenclature is defined in Figure 1; hatched atoms are for the less favored rotamer (occupancy factor 0.38). Listings of hydrogen atom coordinates (calculated), anisotropic thermal parameters, and observed and calculated structure factor amplitudes can be found in the Supplementary Material. Computational details are given in ref 21. The figures were drawn with ORTEP.[22]

(19) The occupancy factor sum for high and low occupancy factor "rotamers" was constrained to unity.

(20) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(21) Computations were done with ANUCRYS[22] and SHELX programs on the UNIVAC 1100/82 computer of the Australian National University Computer Services Centre.

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Table II. Refined Atomic Coordinates (×10^4) for *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (**2**)

atom	x/a	y/b	z/c
Pt	8310 (0)	420 (0)	1368 (0)
P(1)	8572 (1)	2190 (2)	1022 (1)
P(2)	8002 (1)	−1337 (2)	1717 (1)
O(1)	10004 (3)	675 (5)	1861 (2)
O(2)	8904 (4)	1076 (6)	2371 (2)
C(1)	7531 (5)	−4 (7)	765 (3)
C(2)	6625 (5)	172 (7)	729 (3)
C(3)	6127 (6)	−178 (9)	317 (4)
C(4)	6509 (8)	−746 (9)	−64 (4)
C(5)	7418 (7)	−931 (9)	−53 (3)
C(6)	7905 (6)	−548 (7)	364 (3)
C(7)	9134 (5)	790 (7)	1949 (3)
C(11)	7582 (7)	2952 (9)	814 (5)
C(12)	9125 (7)	3218 (9)	1442 (4)
C(13)	9246 (7)	2122 (11)	461 (4)
C(111)	6933 (8)	3210 (12)	1231 (7)
C(121)	9263 (8)	4416 (10)	1276 (5)
C(131)	10149 (8)	1555 (14)	557 (6)
C(21)	8940 (12)	−2067 (28)	1999 (9)
C(22)	7421 (10)	−2407 (13)	1344 (5)
C(23)	7287 (12)	−1151 (27)	2277 (6)
C(211)	9642 (15)	−2321 (21)	1621 (12)
C(221)	7208 (9)	−3575 (14)	1569 (6)
C(231)	6409 (9)	−673 (27)	2141 (6)
C(24)	8449 (22)	−2495 (27)	1283 (11)
C(25)	6877 (20)	−1657 (30)	1804 (13)
C(26)	8543 (22)	−1716 (32)	2293 (12)
C(241)	9478 (20)	−2405 (38)	1199 (11)
C(261)	8465 (24)	−2947 (34)	2482 (14)

Table III. Bond Lengths (Å) and Interbond Angles (deg) in *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (**2**)

Pt–P(1)	2.279 (3)	C(3)–C(4)	1.35 (2)
Pt–P(2)	2.283 (3)	C(4)–C(5)	1.38 (2)
Pt–C(1)	2.071 (8)	C(5)–C(6)	1.42 (1)
Pt–C(7)	2.050 (9)	C(7)–O(1)	1.334 (10)
P(1)–C(11)	1.82 (1)	C(7)–O(2)	1.238 (11)
P(1)–C(12)	1.84 (1)	C(11)–C(111)	1.52 (2)
P(1)–C(13)	1.83 (1)	C(12)–C(121)	1.47 (2)
P(2)–C(21)	1.81 (2)	C(13)–C(131)	1.53 (2)
P(2)–C(22)	1.82 (2)	C(21)–C(211)	1.50 (4)
P(2)–C(23)	1.87 (2)	C(22)–C(221)	1.51 (2)
P(2)–C(24)	1.90 (3)	C(23)–C(231)	1.48 (2)
P(2)–C(25)	1.74 (3)	C(24)–C(241)	1.56 (5)
P(2)–C(26)	1.82 (3)	C(25)–C(231)	1.62 (5)
C(1)–C(2)	1.38 (1)	C(26)–C(261)	1.51 (5)
C(1)–C(6)	1.37 (1)	O–H···O	2.695 (8)
C(2)–C(3)	1.40 (1)		
P(1)–Pt–P(2)	178.2 (1)	C(24)–P(2)–C(26)	102 (2)
P(1)–Pt–C(1)	89.0 (3)	C(25)–P(2)–C(26)	106 (2)
P(1)–Pt–C(7)	91.6 (3)	Pt–C(1)–C(2)	125.4 (7)
P(2)–Pt–C(1)	90.2 (3)	Pt–C(1)–C(6)	120.3 (7)
P(2)–Pt–C(7)	89.3 (3)	C(2)–C(1)–C(6)	114.3 (8)
C(1)–Pt–C(7)	177.0 (4)	C(1)–C(2)–C(3)	123 (1)
Pt–P(1)–C(11)	114.9 (4)	C(2)–C(3)–C(4)	122 (1)
Pt–P(1)–C(12)	113.4 (4)	C(3)–C(4)–C(5)	118 (1)
Pt–P(1)–C(13)	113.6 (5)	C(4)–C(5)–C(6)	118 (1)
C(11)–P(1)–C(12)	104.6 (6)	C(5)–C(6)–C(1)	124 (1)
C(11)–P(1)–C(13)	102.3 (7)	P(1)–C(11)–C(111)	113 (1)
C(12)–P(1)–C(13)	107.0 (6)	P(1)–C(12)–C(121)	119 (1)
Pt–P(2)–C(21)	115.5 (7)	P(1)–C(13)–C(131)	111 (1)
Pt–P(2)–C(22)	117.8 (6)	P(2)–C(21)–C(211)	110 (2)
Pt–P(2)–C(23)	110.5 (6)	P(2)–C(22)–C(221)	119 (1)
C(21)–P(2)–C(22)	107 (1)	P(2)–C(23)–C(231)	110 (1)
C(21)–P(2)–C(23)	99 (1)	P(2)–C(24)–C(241)	113 (2)
C(22)–P(2)–C(23)	104.8 (9)	P(2)–C(25)–C(231)	110 (2)
Pt–P(2)–C(24)	107 (1)	P(2)–C(26)–C(261)	119 (3)
Pt–P(2)–C(25)	116 (1)	Pt–C(7)–O(1)	115.6 (7)
Pt–P(2)–C(26)	119 (1)	Pt–C(7)–O(2)	126.7 (7)
C(24)–P(2)–C(25)	106 (2)	O(1)–C(7)–O(2)	117.7 (8)

Results

Carbon monoxide at room temperature and atmospheric pressure inserts into the Pt–O bond of *trans*-$Pt(OH)(C_6H_5)(PEt_3)_2$

Table IV. Hydroxycarbonyl Group Absorptions (cm^{-1})[a] in the IR Spectra of *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (**2**) and Its ^{13}C-Labeled Analogue (**2a**)

medium (dielectric const[b])	labeling of COOH	ν(OH)	ν(C=O)	ν(C–O)/δ_{OH}
KBr	$^{12}CO_2H$	2643 w	1592 s	1115 s
	$^{13}CO_2H$	2638 w	1553 s	1094 s
benzene (2.3)	$^{12}CO_2H$	2642 w	1633 mw, 1588 s	1110 s
	$^{13}CO_2H$	2625 w	1595 mw, 1552 s	1087 s
dichloromethane (8.9)	$^{12}CO_2H$	3437 w, 2654 w	1661 mw, 1618 s, 1588 s	*c*
	$^{13}CO_2H$	3433 w, 2653 w	1622 mw, 1583 s, 1550 s	1099 s
epichlorohydrin (22.6)	$^{13}CO_2H$	3320 w, 2630 w	1583 s, 1550 m	*c*
2-cyanopyridine (93.8)[d]	$^{12}CO_2H$	2647 w	1623 s	1113 m

[a] ± 2 cm^{-1} (solid state), ± 1 cm^{-1} (solution). [b] Values from Griffiths and Pugh (Griffiths, T. R.; Pugh, D. C. *Coord. Chem. Rev.* **1979**, *29*, 129). [c] Could not be identified. [d] Casteel, J. F.; Sears, P. G. *J. Chem. Eng. Data* **1975**, *20*, 10.

(**1**) to give the hydroxycarbonyl *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (**2**) almost quantitatively as a colorless, crystalline solid (eq 1);

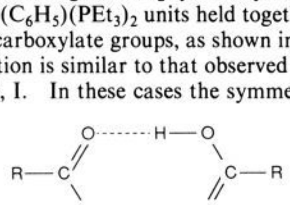
$$Pt(OH)(C_6H_5)(PEt_3)_2 + CO \rightarrow Pt(CO_2H)(C_6H_5)(PEt_3)_2 \quad (1)$$

the ^{13}CO-labeled compound, $Pt(^{13}CO_2H)(C_6H_5)(PEt_3)_2$ (**2a**), is made similarly from ^{13}CO. The reaction is best done in isopentane, from which **2** precipitates in analytically pure form. In other solvents, such as ether, benzene, or dichloromethane, the initially colorless solution turns orange-red, either during the reaction or when solvent is removed under reduced pressure. The red contaminant is easily removed from the main product **2** by washing with isopentane; it may be a platinum(0) cluster formed by a competing reaction in which PEt_3 is displaced by CO.

We have been unable to detect any intermediates in the reaction. In the temperature range −80 °C to −35 °C at a pressure of 150 kPa of ^{13}CO, the only species present, according to ^{13}C and ^{31}P NMR spectroscopy, are **1** and CO. Formation of **2a** begins at −35 °C and is complete at room temperature.

Complex **2** is insoluble in water, but it dissolves readily in most organic solvents. It is slightly air-sensitive, but the solid and its solutions are stable in the absence of air up to 60 °C. The complex is monomeric by osmometry in dichloromethane at concentrations up to 0.03 M. The presence of the CO_2H group is indicated by IR and NMR spectroscopic data and confirmed by single-crystal X-ray analysis.

Structure and Spectroscopic Studies of *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (2). In the solid state, molecules of **2** occur as discrete dimers having exact C_2 symmetry and containing two *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ units held together by closed hydrogen-bonded carboxylate groups, as shown in Figure 2. This mode of association is similar to that observed in many organic carboxylic acids, I. In these cases the symmetry is commonly



I

C_i, and all four oxygen atoms of I are coplanar. In **2** the oxygen atoms define a flattened tetrahedron with "out-of-plane" displacements of ±0.23 Å. The carbon atoms are also slightly out-of-plane (0.10 Å), and the dihedral angle betweeen the two CO_2^- fragments is 31°. The twist serves to displace the (hydrogen) donor oxygen atom [O(1)] by 0.91 Å from the acceptor oxygen [O(2)] lone-pair plane.[24] The angle between the O(1)···O(2) vector and the O(2) lone-pair plane (19.7°) is within the commonly observed range for O–H···O bonds.[25,26] The O–H···O separation of 2.695 (8) Å is only slightly longer than the distance 2.63–2.67 Å commonly found in organic acids.[27] Likewise, the bond lengths

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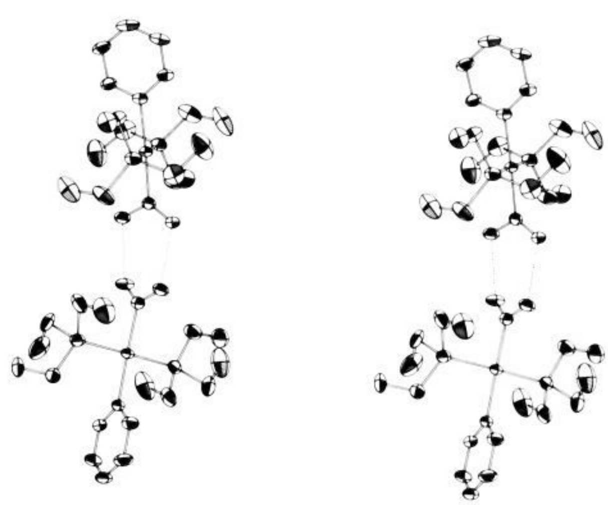

Figure 2. Stereochemistry of the *trans*-$[Pt(CO_2H)(C_6H_5)(PEt_3)_2]_2$ dimer (**2**).

and bond angles in the carboxylate group [r(C=O) 1.238 (11) Å, r(C–O) 1.334 (10) Å, Pt—Ĉ=O 126.7 (7)°, Pt-Ĉ-O 115.6 (7)°, O-Ĉ-O 117.7 (8)°] are close to the corresponding values both in organic acids[27,28] and, except for O—Ĉ=O, in the ethoxycarbonyl complex *trans*-$Pt(CO_2Et)_2(PPh_3)_2$ [r(C=O) 1.228 (7) Å, r(C–O) 1.351 (7) Å, Pt—Ĉ=O 125.9 (5)°, Pt-Ĉ-O 114.6 (4)°, O—Ĉ=O 114.6 (4)°].[29]

As shown in the figures the coordination about each platinum atom is close to square planar,[30] the Pt–P distances [Pt–P(1) = 2.279 (3) Å, Pt–P(2) = 2.283 (3) Å] being similar to those found in arylbis(triethylphosphine)platinum(II) complexes such as $PtCl(C_6H_5)(PEt_3)_2$.[31] The Pt–C_6H_5 and Pt–CO_2H bond lengths of 2.071 (8) and 2.050 (9) Å, respectively, are unexceptional [cf. Pt–C_6H_5 distances of 2.02 (2) Å in *trans*-$PtCl(C_6H_5)(PEt_3)_2$[31] and 2.080 (8) Å in *trans*-$Pt(C_6H_5)_2(PPh_3)_2$,[32] and a Pt–CO_2Et distance of 2.059 (7) Å in $Pt(CO_2Et)_2(PPh_3)_2$].[29]

The dihedral angle between the phenyl ring and the coordination plane Pt, P(1), P(2), C(1), and C(7) is close to 90°, a feature that seems to be general for planar arylmetal complexes, e.g., 86° for the C_6F_5 groups in *trans*-$Ni(C_6F_5)_2(PMe_2Ph)_2$,[33] 78.4° in *trans*-$Pt(C_6H_5)_2(PPh_3)_2$,[32] and 85.8° in *trans*-$Pt(O_2$-*t*-$Bu)(C_6H_5)(PPh_3)_2$.[34] The dihedral angle between the carboxylate

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(30) Results of best plane calculations have been deposited.
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group and the coordination plane, 78.0°, is similar to that (80.8°) in *trans*-$Pt(CO_2Et)_2(PPh_3)_2$.[29] The triethylphosphine ligands each exhibit approximate (180°, 60°, -60°) conformations;[35] bond distances and bond angles therein are unexceptional.

The IR spectra of **2** and of its ^{13}C labeled derivative **2a** are summarized in Table IV. In a KBr disk, the characteristic carboxylate bands of **2** appear at 2643 cm^{-1} (w), 1592 cm^{-1} (s), and 1115 cm^{-1} and are assigned to O–H stretching, C=O stretching, and coupled C–O stretching/O–H deformation modes, respectively.[36] The last two modes are shifted to lower frequency in the spectrum of **2a**, whereas the O–H stretching frequency is almost unaffected, as expected. The position of the ν(OH) band is typical of organic, hydrogen-bonded carboxylic acids (2700–2500 cm^{-1})[36] and is similar to that observed for compounds of the type $Pt(CO_2H)R(P-P)$ (P–P = various aryl ditertiary phosphines).[12] The IR spectra of solutions of **2** and of **2a** in polar, non-hydrogen-bonding solvents show two sets of ν(OH) and ν(C=O) absorptions. One set closely matches the solid-state bands; the other has a ν(OH) band at ca. 3400 cm^{-1} and a ν(C=O) band at ca. 1620 cm^{-1}, both at considerably higher frequency than the corresponding bands in the solid state. The frequency of the ν(OH) band is similar to that in monomeric organic carboxylic acids,[36] so that monomeric and hydrogen-bonded dimeric forms of **2** probably coexist in solution. The C=O stretching frequencies of both monomer and dimer are similar to those reported for other metallacarboxylic acids but are lower by ca. 100 cm^{-1} than those for organic carboxylic acids. Only one ν(C–O)/δ(OH) band is observed in solution at ca. 1000 cm^{-1}, but we do not know whether this is because the monomer/dimer bands overlap or because the dimer band is obscured by strong ligand absorption in this region. The ν(C–O)/δ(OH) band is also at lower frequency than in typical organic carboxylic acids (1320–1211 cm^{-1}).[36]

The monomer–dimer equilibrium in solutions of **2** is influenced in a predictable way by the concentration of **2** and the polarity of the solvent. In benzene the IR spectrum resembles that in the solid state, and bands due to the monomer are absent. Dissociation to monomer is more extensive in epichlorohydrin (dielectric constant 22.6) than in dichloromethane (dielectric constant 8.9). Dilution of a dichloromethane solution of **2** increases the proportion of monomer, e.g., the intensities of the ν(C=O) bands of monomer and dimer are almost equal in 0.45 M solution, but the former is about 25% more intense than the latter in 0.23 M solution. In a polar, hydrogen-bonding solvent such as 2-cyanopyridine (dielectric constant 93.8), the dimer bands disappear completely, and presumably the species present is a monomer which is hydrogen-bonded to the nitrogen atom of the solvent. The IR spectroscopic behavior of **2** thus appears to be intermediate between that of organic carboxylic acids, which are partly hydrogen-bonded even in the gas phase, and the 1-cyclohexenylhydroxycarbonyls $Pt(CO_2H)(C_6H_9)(P-P)$, which are completely monomeric even in dichloromethane.[12] However, the latter compounds may be exceptional, because we have observed recently that the phenyl and methyl hydroxycarbonyls $Pt(CO_2H)R(P-P)$(R = C_6H_5, CH_3) behave similarly to **2** in solution. This difference may arise because the cyclohexenyl ligand is somewhat bulkier and more electron-donating than phenyl or methyl.

In formamide (dielectric constant 109.5) or *N*-methylformamide (dielectric constant ca. 200) the IR spectrum of **2** shows a ν(CO) band at 2092 cm^{-1} (2043 cm^{-1} in the case of **2a**) due to the carbonyl cation $[Pt(C_6H_5)(CO)(PEt_3)_2]^+$ formed by dissociation of hydroxide ion (eq 2). This type of dissociation of a metalla-

$$Pt(CO_2H)(C_6H_5)(PEt_3)_2 \rightleftarrows [Pt(C_6H_5)(CO)(PEt_3)_2]^+ + OH^- \quad (2)$$

carboxylic acid also has been observed in the case of $Fe(\eta^5\text{-}C_5H_5)(CO_2H)(CO)(PPh_3)$, which ionizes in formamide to give $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)]OH$.[2a] Again, the cyclohexenyl complexes $Pt(CO_2H)(C_6H_9)(P-P)$ are exceptional, since they do not show this behavior.[12]

Table V. NMR Data for *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ in Various Solvents[a,b]

solvent	δ_{CO_2H}	δ_{CO_2H} ($^1J_{PtC}$)	δ_P ($^1J_{PtP}$,$^2J_{PC}$)	δ_{Pt}
CD_2Cl_2	7.6[c]	205.1 (827)	10.6 (2755, 11.5)	-4548
toluene-d_8	9.8[d]	206.4 (821)	10.3 (2805, 11.7)	-4552
benzene-d_6	10.8	208.6 (821)	10.4 (2792, 11.0)	nm
acetone-d_6/H_2O (5:1 v/v)		208.6 (822)	nm (11.0)	nm

[a] Carbon-13 chemical shifts recorded on samples enriched to 90% with ^{13}C, chemical shifts being in parts per million to high frequency of Me_4Si, phosphorus-31 chemical shifts in parts per million relative to 85% H_3PO_4 (positive to high frequency), platinum-195 chemical shifts in parts per million relative to external Na_2PtCl_6 in D_2O (positive to high frequency), and coupling constants in hertz. [b] Proton spectra contain multiplets at δ 7.31, 6.95, 6.80 (C_6H_5), 1.61 (PCH_2CH_3), and 1.07 (PCH_2CH_3). [c] 10.2 (-60 °C), 11.2 (-85 °C). [d] 13.3 (-85 °C).

The ^1H NMR spectrum of **2** shows a broad resonance due to the CO_2H proton which appears in the range δ 7–13.5, depending on solvent and temperature (Table V); similar chemical shifts have been reported for other metallacarboxylic acids. The signal sharpens on cooling, but ^{195}Pt satellites are not observed, even at -85 °C. As in the case of $Pt(CO_2H)(C_6H_9)(P-P)$,[12] we do not know whether this is due to self-exchange, to exchange with traces of moisture, or to the small magnitude of $^4J_{PtH}$. The signal disappears completely on addition of D_2O. In the $^{13}C\{^1H\}$ NMR spectrum, the carboxylate carbon appears as a triplet at δ ca. 205 with ^{195}Pt satellites ($^2J_{PC}$ = 11.5 Hz, $^1J_{PtC}$ ca. 820 Hz) (Table V). These values differ considerably from those of the closely related compounds *trans*-$PtCl(CO_2H)(PEt_3)_2$ (δ CO_2H = 173.4, $^1J_{PtC}$ = 1337 Hz)[8] and $Pt(CO_2H)(C_6H_9)(P-P)$ (δ_{CO_2H} = 195.0–196.4, $^1J_{PtC}$ = 1265–1330 Hz),[10] presumably because of the differing ligands trans to the CO_2H group. Related observations have been made on neutral and cationic compounds of the type *trans*-$PtY(CO)L_2$ (L = various tertiary phosphines and arsines). For ligands Y of high trans influence, $^1J_{PtC}$ is in the range 960–990 Hz and δ(^{13}CO) is ca. 180 (cf. δ = 180.5 for free ^{13}CO), whereas for ligands Y of low trans influence, $^1J_{PtC}$ is in the range 1658–1817 Hz and δ(^{13}CO) is 155–165.[37]

The $^{31}P\{^1H\}$ NMR spectrum of **2** consists of a singlet with ^{195}Pt satellites (Table V) and confirms that the PEt_3 ligands are equivalent and mutually trans. These resonances are doubled by coupling to ^{13}C in the spectrum of **2a**. The ^{195}Pt NMR spectrum of **2a** consists of a triplet of doublets arising from the X part of an A_2MX spin system, the values of $^1J_{PtP}$ and $^1J_{PtC}$ being identical with those derived from the ^{31}P and ^{13}C NMR spectra, respectively. The values of δ_P and δ_{Pt} are in the ranges expected for platinum(II)–triethylphosphine complexes.[38,39]

Chemical Reactivity of 2. Like the hydroxycarbonyls $Pt(CO_2H)(C_6H_9)(P-P)$,[12] **2** fails the standard tests for organic carboxylic acids; e.g., it does not dissolve in 5% aqueous KOH, and it neither dissolves in nor reacts with 5% aqueous $KHCO_3$. It also does not form salts with tertiary amines such as triethylamine, 2-cyanopyridine, and 1,8-bis(dimethylamino)naphthalene. Its chemistry is dominated by the facile cleavage of the C–O bond to give the carbonyl cation *trans*-$[Pt(C_6H_5)(CO)(PEt_3)_2]^+$, a reaction that is characteristic of metal hydroxycarbonyls. This cation is formed, as its BF_4 salt, when **2** is treated with $HBF_4{\cdot}OEt_2$. The corresponding chloride salt can be identified as the product of reaction of **2** with HCl at low temperature, but it loses CO at room temperature to give *trans*-$PtCl(C_6H_5)(PEt_3)_2$. Reaction of **2** with H_2S gives *trans*-$Pt(SH)(C_6H_5)(PEt_3)_2$. Like $Pt(CO_2H)(C_6H_9)(P-P)$, **2** reacts completely at room temperature with

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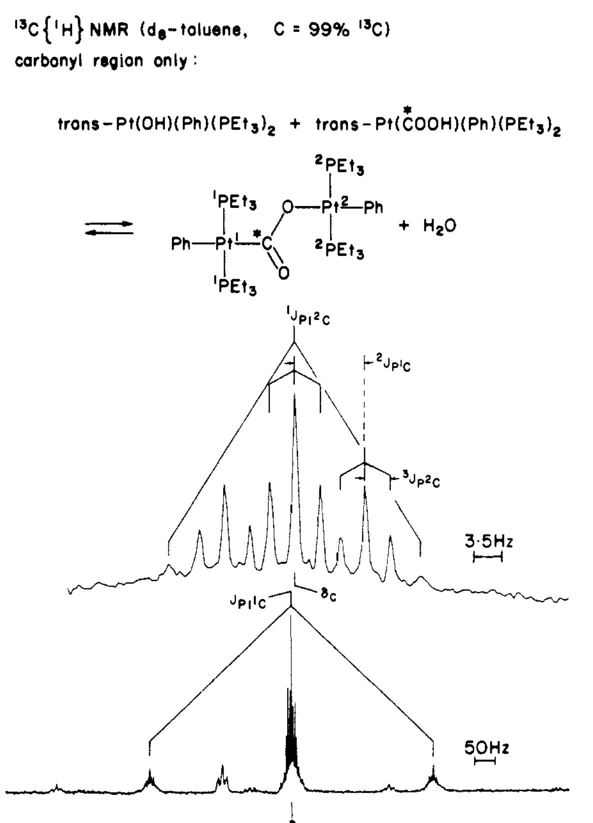
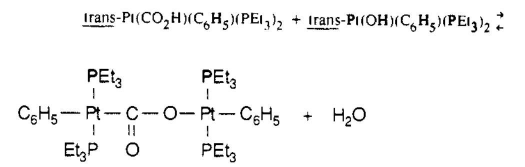


Figure 3. ^{13}C NMR pattern, measured at 50.29 MHz, due to the carbonyl group of $(C_6H_5)(Et_3P)_2Pt(\mu\text{-}^{13}CO_2)Pt(C_6H_5)(PEt_3)_2$ (**5a**) formed in situ from $Pt(^{13}CO_2H)(C_6H_5)(PEt_3)_2$ (**2a**) and $Pt(OH)(C_6H_5)(PEt_3)_2$ (**1**) in toluene-d_8.

methanol and with dimethylamine to give the corresponding methoxycarbonyl and dimethylcarbamoyl derivatives, *trans*-$Pt(CO_2Me)(C_6H_5)(PEt_3)_2$ (**3**) and *trans*-$Pt(CONMe_2)(C_6H_5)(PEt_3)_2$ (**4**), respectively. The IR and NMR spectroscopic data which confirm these formulations are given in the Experimental Section. Solutions of **2a** exchange readily with CO to give **2**, a reaction that may proceed either via a five-coordinate intermediate. $Pt(OH)(C_6H_5)(CO)(PEt_3)_2$ or a four-coordinate salt $[Pt(C_6H_5)(CO)(PEt_3)_2]OH$.

In view of its lack of conventional acidic properties, it is surprising that **2** reacts readily with its precursor **1** in toluene to give a dimeric platinum(II) complex **5** that contains bridging carbon dioxide (eq 3); the ^{13}C-labeled compound **5a** is obtained similarly



(3)

5

from **2a**. The formulation of **5** is based mainly on its NMR parameters, which are summarized in Table VI. The formation of **5** is reversible: when equimolar amounts of **1** and **2** are mixed, all four species of eq 3 can be observed by NMR or IR spectroscopy, although **5** is the main platinum-containing species present. Removal of water by distillation gives **5** almost quantitatively, whereas if the mixture is treated with CO, the only product formed is the hydroxycarbonyl complex **2** as a result of selective removal of the hydroxo complex **1**. Pyrolysis of **2** at ca. 100 °C also gives **5** in high yield, together with ca. 0.5 mol of CO per mol of Pt. This reaction presumably proceeds by initial elimination of CO from **2** to give **1** (the reverse of eq 1) and subsequent reaction of **1** with unchanged **2**.

The ^1H NMR spectrum of **5** differs from that of **2** only in the absence of the CO_2H resonance, but the $^{13}C\{^1H\}$ NMR spectrum

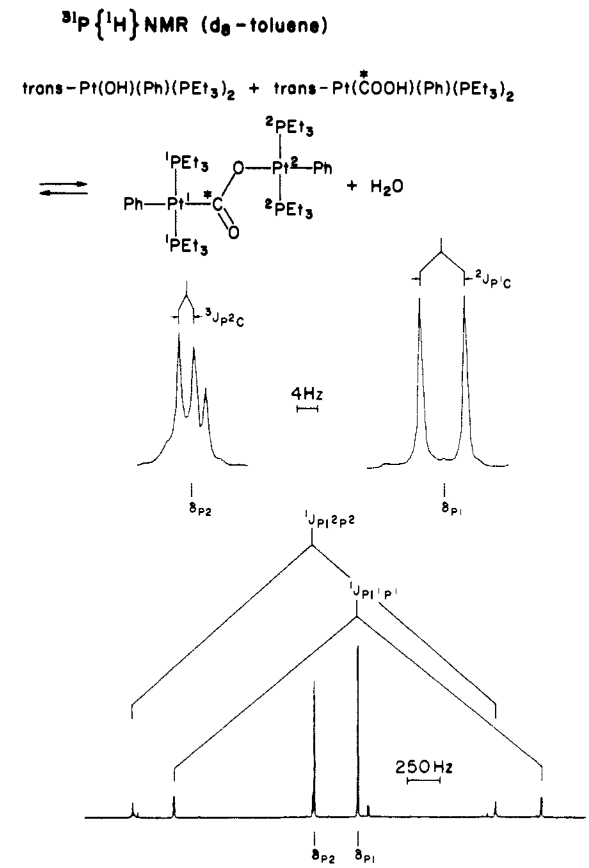
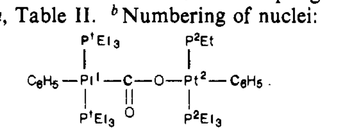


Figure 4. $^{31}P\{^1H\}$ NMR spectrum at 80.98 MHz of $(C_6H_5)(Et_3P)_2Pt(\mu\text{-}^{13}CO_2)Pt(C_6H_5)(PEt_3)_2$ (**5a**) in toluene-d_8.

Table VI. Selected NMR Parameters of $[trans\text{-}Pt(C_6H_5)(PEt_3)_2]_2(\mu\text{-}^{13}CO_2)$ (**5a**)

parameter	solvent: CD_2Cl_2	solvent: toluene-d_8
δ_C	201.0	200.1
δ_{P^1}	11.2	11.6
δ_{P^2}	16.4	15.9
δ_{Pt^1}	−4480	−4472
δ_{Pt^2}	−4060	−4063
$^1J_{Pt^1C}$	707	727
$^1J_{Pt^2C}$	34.7	32
$^1J_{Pt^1P^1}$	3035	3052
$^1J_{Pt^2P^2}$	2978	2998
$^2J_{P^1C}$	9.0	9.0
$^3J_{P^2C}$	3.4	3.2
$^3J_{PtPt}$	219	201

[a] Conventions used for chemical shifts and coupling constants are as given in footnote *a*, Table II. [b] Numbering of nuclei:



of **5a** exhibits a multiplet in the organic carbonyl region at δ ca. 201 which must be due to a quaternary carbon atom, since its appearance in the proton-coupled spectrum is unchanged. At first sight the signal looks like a triplet of triplets flanked by ^{195}Pt satellites (J_{PtC} ca. 700 Hz), but closer inspection reveals the presence of a second set of ^{195}Pt satellites with a much smaller value of J_{PtC} (ca. 32 Hz) (Figure 3). This suggests that **5** contains a carbonyl atom that is coupled to two different pairs of phosphorus atoms and to two inequivalent platinum nuclei, i.e., that the carbon atom is the A part of an AM_2N_2XY spin system (M, N = ^{31}P; X, Y = ^{195}Pt). The magnitude of the larger J_{PtC} indicates that the carbonyl carbon atoms is bound directly to one of the platinum atoms. The $^{31}P\{^1H\}$ NMR spectrum of **5a** (Figure 4) consists of a pair of doublets each flanked by ^{195}Pt satellites ($^1J_{PtP}$

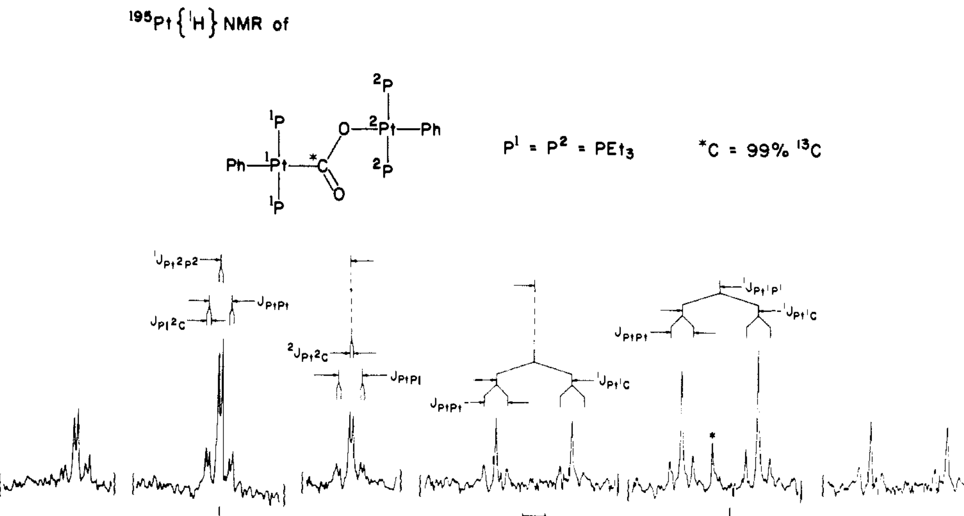


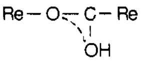
Figure 5. $^{195}Pt\{^1H\}$ NMR spectrum at 42.8 MHz of $(C_6H_5)(Et_3P)_2Pt(\mu\text{-}^{13}CO_2)Pt(C_6H_5)(PEt_3)_2$ (**5a**) in toluene-d_8.

ca. 3000 Hz) due to the M_2N_2 part of the system ($J_{MN} = 0$). Thus there are two distinct pairs of mutually trans PEt_3 ligands which are coupled differently to the carbonyl carbon atom. The ^{13}C and ^{31}P NMR spectra therefore show unequivocally that **5** contains two *trans*-$C_6H_5Pt(PEt_3)_2$ fragments bridged unsymmetrically by a ligand containing a carbonyl carbon atom but no hydrogen atom, and the only reasonable candidate for this ligand is CO_2^{2-}. The ^{195}Pt NMR spectrum of **5a** (Figure 5) confirms the presence of two different ^{195}Pt nuclei and reproduces the $^1J_{PtC}$ and $^1J_{PtP}$ values derived from the ^{13}C and ^{31}P NMR spectra. Further, the small coupling between the two ^{195}Pt nuclei (ca. 200 Hz) suggests that they are not bound directly, although this criterion must be applied with caution.[39]

The characteristic CO_2H absorptions are absent from the IR spectrum of **5** in CH_2Cl_2, but there are three new bands assignable to C–O vibrations of the CO_2^{2-} ligand at 1495 cm^{-1} (s), 1290 cm^{-1} (m), and 1190 cm^{-1} (vs). The first two of these bands are not present in the IR spectrum of the ^{13}C-labeled material **5a**, their isotopically shifted counterparts probably being masked by strong PEt_3 absorptions at 1457 and ca. 1260 cm^{-1}. The band at 1190 cm^{-1} in the spectrum of **5** shifts to 1163 cm^{-1} in that of **5a**.

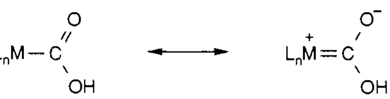
Discussion

This work has provided the first structural characterization of a metallacarboxylic acid in which the CO_2H group acts as a monodentate, C-donor ligand. The only other metallacarboxylic acid to be studied crystallographically is $Re_3(CO)_{14}(\mu_3\text{-}CO_2H)$, in which a five-electron donor CO_2H group is bound through carbon to one rhenium atom and by the two oxygen atoms to the other two rhenium atoms.[40] The C–O bond lengths in the CO_2H unit in this compound are equal, within experimental error, at 1.294 (24) Å, whereas those in **2** are significantly different (see above). The hydrogen atom in $Re_3(CO)_{14}(\mu_3\text{-}CO_2H)$ could not be located, but the reported ν(OH) frequency of 3700 cm^{-1} suggests that O–H···O bridging is absent. These differences from the behavior of **2** indicate that the CO_2H group can coordinate in a variety of ways. For example, a compound of empirical formula $Re(CO)_5OH$ obtained by the action of aqueous base on $Re(CO)_5BF_4$ has been suggested,[41] on the basis of its IR spectrum, to contain the unit, shown below. Nevertheless, it seems probable that most of the metallacarboxylic acids cited in the introduction are structurally similar to **2**.



(40) (a) Balbach, B. K.; Helus, F.; Oberdorfer, F.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 470. (b) Oberdorfer, F.; Balbach, B.; Ziegler, M. L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 157.
(41) Beck, W.; Raab, K.; Nagel, U.; Steimann, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 526.

Although the C═O and C–O bond lengths in the dimeric hydrogen-bonded unit of **2** are close to those in typical organic carboxylic acids, the fact that the O–H···O separation is at the upper end of the commonly observed range may correlate with the ease of dissociation of **2** into neutral monomers and with the lack of conventional proton donor behavior. These effects may result from strong electron donation from the phenyl and PEt_3 ligands through platinum to the hydroxycarbonyl group, which can be expressed in terms of a dipolar resonance contribution to the bonding in L_nMCO_2H. As noted earlier,[12] this explanation



is supported by the observation that the ν(C═O) frequency in most metallacarboxylic acids is ca. 100 cm^{-1} lower than that in typical organic carboxylic acids, but, surprisingly, the Pt–CO_2H bond is only slightly shorter than the Pt–C_6H_5 bond. A similar dipolar resonance contribution has been invoked to account for the low C═O frequencies in metal carbamoyls relative to those in carboxamides. The idea received some support from the observation that the Mn–C(carbamoyl) bond distance of 2.07 Å in $Mn(CONHCH_3)(CO)_4(NH_2CH_3)$ is less than the calculated value of 2.15 Å.[42] However, more recently, it has been shown that the Fe–C(carbamoyl) distance in $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ (μ-$CONH(CH_2)_2NHCO$) [1.991 (6) Å] is typical of Fe–C(sp^2) bond distances.[43]

The insertion of CO into a Pt–OH bond can be used to make platinum(II) hydroxycarbonyls containing either cis bidentate bis(tertiary phosphines) or trans monodentate tertiary phosphines. However, attempts to isolate hydroxycarbonyls containing triphenylphosphine or tricyclohexylphosphine have been frustrated by the formation of platinum(0) clusters, which presumably arise by a completing displacement of tertiary phosphine by CO. There is no evidence for the presence of discrete four- or five-coordinate platinum(II) carbonyl intermediates or of free or coordinated formate ion. Complete dissociation of OH^- from the coordination sphere is therefore unlikely, and formation of **2** probably entails concerted coordination of CO and labilization of the Pt–OH bond.

The insertion of CO into the Pt–OH bond of **1** is reversible, as is clear from the formation of **5** and 0.5 mol of CO when **1** is heated. This mode of decomposition differs from that observed in most other metallacarboxylic acids viz. formation of a metal hydride and elimination of CO_2, though the conditions (neutral or basic) under which this "normal" decomposition route is followed vary considerably for different systems. The only other

(42) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.
(43) Lindsay, A. J.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1984**, *3*, 1523.

example to our knowledge of thermal elimination of CO from a metallacarboxylic acid is the previously mentioned compound $[Re(CO_2H)(CO)_4]_2$, which gives $[Re(CO)_3OH]_4$ and CO at 100–150 °C.[41] We[12] have suggested previously that complexes such as **2** and $Pt(CO_2H)(C_6H_9)(P\text{–}P)$ do not lose CO_2 because they do not contain a ligand, such as Cl, PPh_3, or CO, that can dissociate readily and reversibly from the coordination sphere and thus cannot easily accommodate the ligands H^- and CO_2 that would be generated by β-hydride migration. In addition, the complexes are not sufficiently acidic to allow deprotonation, loss of CO_2, and reprotonation at the metal atom. The surprising and unexpected feature is that **2** is nevertheless sufficiently acidic to donate a proton to the strongly basic hydroxoplatinum(II) complex **1** in a kind of esterification reaction to give the μ_2-CO_2 complex **5**.

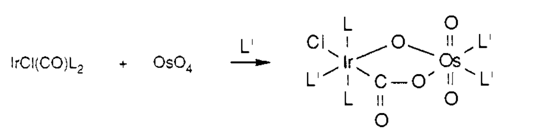
There are relatively few well-characterized complexes in which CO_2 bridges two transition-metal centers,[44] and it is difficult to assign the bridging mode of CO_2 in **5** unambiguously by comparison of its characteristic IR bands (1495, 1290, and 1190 cm^{-1}) with those of related compounds. Thus, the $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ bonded complex **6** (eq 4) has C=O and C–O stretching bands at 1593 and 1022 cm^{-1}, respectively,[45] whereas the $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$ bonded complex **7** (eq 5) has corresponding bands at 1350 and 1278 cm^{-1}.[46] The structurally characterized $\mu(\eta^1\text{-C}:\eta^2\text{-O,O}')$ complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO_2SnPh_3)$ has CO_2 bands at 1395 and 1188 cm^{-1}, whereas in its $\mu(\eta^1\text{-C}:\eta^1\text{-O,O}')GePh_3$ analogue corresponding bands appear at 1545 and 1048 cm^{-1}.[47] An X-ray study of the complex $[Pt(CH_3)(dppp)]_2(\mu\text{-}CO_2)$, prepared from $Pt(OH)(CH_3)(dppp)$ and $Pt(CO_2H)(CH_3)(dppp)$ (dppp = $Ph_2P(CH_2)_3PPh_2$), has shown the presence of a $\mu(\eta^1\text{-C}:\eta^1\text{-O})CO_2$ ligand,[48] and the same is likely to be true for **5**.

(44) Reviews of transition-metal–CO_2 chemistry: (a) Kolomnikov, I. S.; Grigoryan, M. Kh. *Russ. Chem. Rev. (Eng. Transl.)* **1978**, *47*, 334. (b) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79. (c) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, p 225. (d) Ito, T.; Yamamoto, A. In *Organic and Bio-organic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Wiley: New York, 1982; Chapter 3. (e) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (f) Behr, A. In *Catalysis in C_1 Chemistry*; Keim, W., Ed.; D. Reidel: Boston, 1983; pp 169–219.

(45) Audett, J. D.; Collins, T. J.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1982**, *104*, 7352.

(46) Tso, C. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6069.

(47) Senn, D. R.; Gladysz, J. A.; Emerson, K.; Larsen, R. D. *Inorg. Chem.* **1987**, *26*, 2737.



(4)

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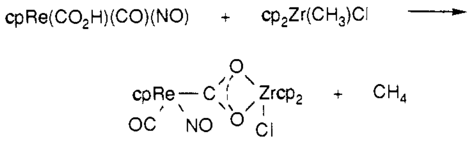
(L = PPh_3; L' = 4-*t*-BuC_5H_4N)



(5)

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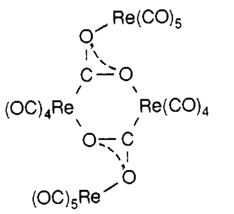
We know of only one other case in which a metallacarboxylic acid decomposes to give a μ-CO_2 complex. The complex $Re(CO)_5OH$ (see above) loses water at 20 °C in acetone to give the μ_3-CO_2 complex **8**.[41] This behavior may be more common than suspected hitherto, especially with hydroxycarbonyls of the 5d-elements.



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Registry No. 1, 76124-93-1; **2**, 114691-13-3; **2a**, 115650-78-7; **3**, 115650-83-4; **4**, 115650-84-5; **5**, 115650-85-6; **5a**, 115650-86-7; *trans*-$[Pt(C_6H_5)(^{13}CO)(PEt_3)_2]BF_4$, 115650-80-1; *trans*-$[Pt(C_6H_5)(^{13}CO)(PEt_3)_2]Cl$, 115650-81-2; *trans*-$Pt(SH)(C_6H_5)(PEt_3)_2$, 115650-82-3.

Supplementary Material Available: Listings of hydrogen atom coordinates (calculated) and anisotropic thermal parameters for *trans*-$Pt(CO_2H)(C_6H_5)(PEt_3)_2$ (3 pages); listing of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

(48) Bennett, M. A.; Ditzel, E. J.; Grundy, K. R.; Robertson, G. B.; Rokicki, A., unpublished work.