Synthesis and Structural Characterization of an Authentic Platinum(IV) Carbonyl Compound

Juan Forniés,* Miguel A. Gómez-Saso, Antonio Martín, Francisco Martínez, Babil Menjón, and Javier Navarrete

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza−Consejo Superior de Investigaciones Científicas, E-50009 Zaragoza, Spain

Summary: The oxidative addition of Br$_2$ to [NBu$_4$]$_2$[Pt-(C$_6$F$_5$)$_4$] followed by halide extraction with AgClO$_4$ in the presence of CO gave [NBu$_4$][trans-Pt^{IV}(C$_6$F$_5$)$_4$Br(CO)], the first Pt(IV) carbonyl derivative to be structurally characterized. It is demonstrated that the previously reported [NEt$_4$][PtBr$_3$H$_2$(CO)] complex is, in fact, the Pt-(II) derivative [NEt$_4$][PtBr$_3$(CO)].

Introduction

Carbon monoxide is one of the most common and useful ligands in organotransition metal chemistry.[1] Its ability to bind to low-valent metals was at first puzzling, although it could be satisfactorily explained by postulating the existence of a synergic bond with two components: carbon-to-metal σ-donation and metal-to-carbon π-back-donation.[2,3] For a long time, this bonding model was found to apply to almost every stable metal carbonyl compound, and as a result of this, the idea emerged that π-back-donation was needed for metal carbonyls to be stable. This idea is, however, not upheld as an increasing number of metal carbonyl compounds in which CO acts as a mainly σ-donor ligand[4] are being reported. These examples appear when the electrons of the metal center are unavailable for π-back-bonding with CO, as is the case, for instance, in d^0 metal ions[6,7] or in late- and post-transition metals in a medium-to-high oxida-

tion state.[8,9] For a given metal the availability of electron density decreases as its oxidation state increases, and this trend is normally evidenced by an increase in ν(CO) values.

The first reported metal carbonyl compound was the Pt(II) derivative [Pt$_2$(μ-Cl)$_2$Cl$_2$(CO)$_2$].[10] Since then many carbonyl compounds of platinum in a oxidation state of II or lower have been described,[11] whereas only a few Pt(IV) carbonyl compounds have been reported.[12−16] This latter category comprises a series of hydrido−carbonyl derivatives of Pt(IV),[14] including the structurally characterized[15] complex [NEt$_4$][PtBr$_3$H$_2$(CO)]. In

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this paper, we demonstrate that the latter complex is, in fact, the Pt(II) carbonyl compound [NEt$_4$][PtBr$_3$(CO)]. Moreover, we also report on the synthesis and first structural characterization of an authentic Pt(IV) carbonyl compound which contains a mainly σ-donor CO ligand.

Experimental Section

Methods for preparing K$_2$[PtCl$_6$][17] and [NBu$_4$]$_2$[Pt(C$_6$F$_5$)$_4$][18] as well as the instrumentation[19] used to characterize complexes **1** and **2** have been published elsewhere.

Preparation of [NEt$_4$][PtBr$_3$(CO)] (1). *Method a.* The procedure to prepare [NEt$_4$][PtBr$_3$H$_2$(CO)] was repeated as reported in ref 14a. The product obtained was identified as **1**. *Method b.* A suspension of K$_2$[PtCl$_6$] (0.675 g, 1.388 mmol) in a mixture of 90% formic acid (15 mL) and concentrated hydrobromic acid (5 mL) also containing NEt$_4$Br (0.624 g, 2.97 mmol) was refluxed until it became a clear, yellow solution (*ca.* 4 h). Then the solution was evaporated, and the yellow solid formed was filtered, washed with small amounts (3 mL each) of cool water, 2-PrOH, and Et$_2$O, and eventually dried (0.772 g, 94% yield). Anal. Found (Calcd for C$_9$H$_{20}$Br$_3$NOPt): C, 17.97 (18.23); H, 3.31 (3.40); N, 2.28 (2.36). IR (Nujol): ν-(C≡O) 2088 cm^{-1}. MS (FAB$^-$): *m/z* 460 [PtBr$_3$(CO)]$^-$.

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of a layer of *n*-hexane (20 mL) into a solution of 25 mg of **1** in 5 mL of CH$_2$Cl$_2$ at 5 °C.

Crystal Data and Data Collection Parameters. C$_9$H$_{20}$Br$_3$NOPt, M_w = 593.08, triclinic, a = 7.300(5) Å, b = 9.236(6) Å, c = 11.625(8) Å, α = 88.32(6)°, β = 88.23(2)°, γ = 82.28(8)°, U = 776.0(9) Å^3 (by least-squares refinement on diffractometer angles from 72 centered reflections, including Friedel pairs, 20.6° < 2θ < 34.9°), T = 173(1) K, space group $P\bar{1}$, graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å, Z = 2, D_c = 2.538 g cm^{-3}, F(000) = 544, yellow; approximate crystal dimensions of 0.27 × 0.23 × 0.20 mm; μ(Mo Kα) = 167.4 cm^{-1}, semiempirical absorption correction based on ψ scans, transmission factors 0.356−0.263; Siemens STOE/AE2 four-circle diffractometer, ω/θ scans, data collection range 1.75° < θ < 24.99°, +h, ±k, ±l, three standard reflections showed no significant variation in intensity; 2901 reflections measured, 2667 unique (R_{int} = 0.0216) which were used in all calculations.

Structure Solution and Refinement. The structure was solved by Patterson and Fourier methods and refined anisotropically by full-matrix least squares on F^2 (program SHELXL 93).[20] Hydrogen atoms were included using a riding model or as rigid methyl groups. The weighting scheme was $w = [\sigma^2(F_o^2) + (0.057P)^2]^{-1}$, where $P = {}^1/_3[\max\{F_o^2,0\} + 2F_c^2]$. The final wR2($F^2$) was 0.0878, with conventional R(F) 0.0375 (R factors defined in ref 20), for 140 parameters, gof = 1.096, max Δ/σ = 0.001, max $\Delta\rho$ = 1.14 e Å^{-3} (−2.39 e Å^{-3}) located at less than 1.39 Å from the platinum atom.

Preparation of [NBu$_4$][*trans*-Pt(C$_6$F$_5$)$_4$Br(CO)] (2). Br$_2$ (0.3 mmol) in CCl$_4$ was added to a CH$_2$Cl$_2$ (15 mL) solution of [NBu$_4$]$_2$[Pt(C$_6$F$_5$)$_4$] (400 mg, 0.297 mmol) at −60 °C. After 15 min, AgClO$_4$ (62 mg, 0.3 mmol) was added and a slow stream of CO was passed through the suspension while the temperature was allowed to rise to 0 °C. The suspension then was filtered, and the filtrate was concentrated to *ca.* 3 mL. By adding cold 2-PrOH, a white solid was obtained, which was filtered and washed with 2-PrOH and *n*-hexane (54 mg, 15%

yield). Anal. Found (Calcd for C$_{41}$H$_{36}$BrF$_{20}$NOPt): C, 40.07 (40.57); H, 2.92 (2.99); N, 1.81 (1.15). IR (Nujol): ν(C≡O) = 2166 cm^{-1}. ^{19}F NMR (282.2 MHz, CDCl$_3$, 20 °C): δ = −110.0 (^3J(^{195}Pt,F) = 130 Hz, 4 F, *o*-F), −115.3 (^3J(^{195}Pt,F) = 77 Hz, 4 F, *o*-F), −160.2 (4 F, *p*-F), −163.1 (4 F, *m*-F), −164.2 (4 F, *m*-F).

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of a layer of *n*-hexane (20 mL) into a solution of 30 mg of **2** in 5 mL of CH$_2$Cl$_2$ at −30 °C.

Crystal Data and Data Collection Parameters. C$_{42.25}$H$_{38.5}$BrCl$_{2.5}$F$_{20}$NOPt, M_w = 1319.8, triclinic, a = 12.304-(13) Å, b = 13.265(14) Å, c = 16.79(2) Å, α = 89.1(1)°, β = 68.20(9)°, γ = 83.36(8)°, U = 2526.39 Å^3 (by least-squares refinement on diffractometer angles for 36 centered reflections in the range 15° < 2θ < 22°), T = 200 K, space group $P\bar{1}$, graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å, Z = 2, D_c = 1.59 g cm^{-3}, F(000) = 1336, colorless with dimensions of 0.3 × 0.2 × 0.2 mm, μ(Mo Kα) = 36.7 cm^{-1}, semiempirical absorption correction based on ψ scans, transmission factors 0.3369−0.5204; Siemens STOE/AE2 four-circle diffractometer, ω−θ scans, data collection range 4.0° < 2θ < 48.0°, +h, ±k, ±l, three standard reflections showed no significant variation in intensity; 8347 reflections measured, 7926 unique (R_{int} = 0.0514) giving 3361 data with F > 5.0σ(F).

Structure Solution and Refinement. The structure was solved and developed by Patterson and Fourier methods (program SHELXTL-PLUS).[21] All non-hydrogen atoms except the solvent atoms (CH$_2$Cl$_2$) were assigned anisotropic displacement parameters. Four atomic sites in an interstitial zone were modeled as a pair of partially occupied disordered CH$_2$-Cl$_2$ molecules. A common isotropic displacement parameter was refined for the two Cl atoms of each disordered CH$_2$-Cl$_2$ moiety. Loose restraints to equality were applied to the C−Cl distances and Cl−C−Cl angles in only one of the solvent molecules. The data-to-parameter ratio in the final refinement was 5.5. The weighting scheme was $w = [\sigma^2(F) + 0.004056F^2]^{-1}$. The final wR2 was 0.0569, with conventional R = 0.0553 (R factors defined in ref 21), for 605 parameters, gof = 1.0791, max Δ/σ = 0.002, max $\Delta\rho$ = 1.18 e Å^{-3} (−1.38 e Å^{-3}).

Results and Discussion

It had been reported that the carbonylation of K$_2$-[PtCl$_4$] in dilute hydrochloric or hydrobromic solutions gave [Pt(CO)$_2$]$_n$,[22] whose treatment with an excess of Fe$_2$(SO$_4$)$_3$ resulted in formation of hydridocarbonyl complexes of formula PtX$_2$H$_2$(CO), where X = Cl or Br.[14] The analogous iodo-derivative was prepared by treating PtCl$_2$H$_2$(CO) with an excess of KI.[14a] These neutral species take up one further equivalent of X$^-$, yielding the corresponding anions [PtX$_3$H$_2$(CO)]$^-$.[14] The formulation of these compounds relied mainly on analytical and IR spectroscopic data, except for complex [NEt$_4$]-[PtBr$_3$H$_2$(CO)] which was also studied by X-ray diffraction methods.[15] There are, however, a number of anomalous features associated with the IR data:[14] (1) the ν(CO) values are too low, considering the high oxidation state of the metal center; (2) with the exception of X = Cl, the ν(CO) shifts observed on going from the neutral to the anionic species are the opposite of what would be expected for an increase in negative charge; and (3) one of the given ν(Pt−H) absorptions appears to *invariably* coincide with the ν(CO) band, regardless of the global charge and of the nature of X.

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Table 1. Comparative IR Vibrational Data (in cm^{-1}) of Some Halocarbonyl Complexes of Platinum

	$\nu(C{\equiv}O)$			$\nu(Pt{-}H)^a/\nu(^{13}C{\equiv}O)^b$		
	X = Cl	X = Br	X = I	X = Cl	X = Br	X = I
$[Pt^{IV}X_3H_2(CO)]^{-,a}$	2100	2090	2080	2055	2035	2025
$[Pt^{II}X_3(CO)]^{-,b}$	2096.5	2089.5	2078	2050	2043	2029
$[Pt^{IV}X_2H_2(CO)]^a$	2125	2085	2050			
$[Pt^{II}_2X_4(CO)_2]^c$	2146	2135	2109			

^{a} See ref 14a. ^{b} See ref 26. ^{c} See ref 32.

These anomalies led us to question both the oxidation state assigned to the Pt center and the presence of hydride ligands in those complexes. We, therefore, decided to check the formulation of the best characterized compound of that family, *i.e.*, [NEt$_4$][PtBr$_3$H$_2$(CO)] for which the X-ray structure had also been reported. However, X-ray diffraction is not the most suitable technique for unambiguously detecting and locating hydride substituents in metal complexes.[23] For hydride location by X-ray diffraction to be reasonably reliable, good quality crystals and careful data collection (preferably at low temperature) are generally required.[24] The X-ray diffraction analysis of [NEt$_4$][PtBr$_3$H$_2$(CO)] gave large esd values, even in the cell parameters and a final $R = 0.105$.[15] Hence, the statement that "the coordination of Pt atom in the complex anion is octahedral with 2 H atoms in trans-position" should be considered with caution.

We have repeated the published synthesis of [NEt$_4$][Pt^{IV}Br$_3$H$_2$(CO)][14a] and have obtained a solid sample with the following spectroscopic properties: (1) the IR spectrum is identical to that of a sample of [NEt$_4$][Pt^{II}Br$_3$(CO)] (**1**);[25] the absorption originally attributed to a ν(Pt−H) mode is indeed very weak and can be assigned to the ν(^{13}CO) vibration[26] (Table 1). (2) The ^{1}H NMR spectrum does not contain any hydride signal, at least in the range registered (+10 to −30 ppm). (3) The chemical shift of the ^{195}Pt NMR signal coincides with that reported for [Pt^{II}Br$_3$(CO)]$^-$;[27] moreover, the signal appears as a singlet instead of as the triplet expected for a dihydride species. Additionally, the X-ray crystal structure was redetermined, giving cell parameters which are virtually identical to those previously reported for [NEt$_4$][Pt^{IV}Br$_3$H$_2$(CO)],[15] as shown in Table 2. When comparing the two sets of parameters, the different choice of cell axes in each case should be noted. An ellipsoid drawing of the anion of **1** is given in Figure 1, and a selection of bond distances and angles is shown in Table 3. The Pt(II) center is in the usual square-planar environment with all four angles between adjacent substituents very close to the ideal 90° value. The Pt−Br distances are very similar, regardless of the different *trans* influence that would be expected for the

Table 2. Comparative Crystal Parameters of Bromocarbonylplatinate Derivatives

	[NEt$_4$][Pt^{IV}Br$_3$H$_2$(CO)]^a	[NEt$_4$][Pt^{II}Br$_3$(CO)]^b
a (Å)	9.44(2)	7.300(5)
b (Å)	11.92(3)	9.236(6)
c (Å)	7.58(2)	11.625(8)
α (deg)	90.0(5)	88.32(6)
β (deg)	98.2(5)	88.23(2)
γ (deg)	90.0(5)	82.28(8)
Z	2	2
space group	$P\bar{1}$	$P\bar{1}$

^{a} See ref 15. ^{b} This work.
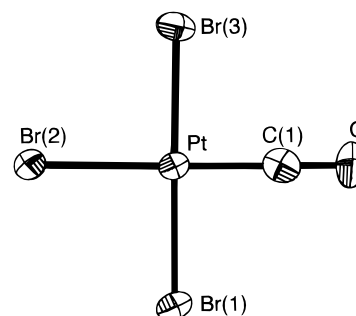
Figure 1. Thermal ellipsoid diagram of the anion of **1**.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for the Anion of 1

Pt−Br(1)	2.444(2)	Pt−C(1)	1.830(10)
Pt−Br(2)	2.434(2)	C(1)−O	1.159(12)
Pt−Br(3)	2.432(2)		

Br(1)−Pt−Br(2)	90.72(7)	Br(1)−Pt−Br(3)	176.93(4)
Br(2)−Pt−Br(3)	90.46(7)	Br(2)−Pt−C(1)	175.7(3)
Br(1)−Pt−C(1)	90.0(3)	Pt−C(1)−O	177.7(8)
Br(3)−Pt−C(1)	89.0(3)		

Br$^-$ and CO ligands.[28] These Pt−Br distances do not significantly deviate from the mean value reported for terminal Pt−Br bonds in four-coordinate Pt(II) complexes (2.438 Å).[29] The Pt−C(1)−O unit is almost linear (174(2)°), and the Pt−C(1) distance (1.830(10) Å) is in the range of Pt−CO distances observed in four-coordinate carbonyl derivatives of Pt(II) (1.75−1.98 Å).[30] The C(1)−O distance (1.159(12) Å) is near to the upper end of the corresponding range of C≡O distances in the same kind of complexes (1.06−1.18 Å).[30] All of the distances and angles in [NEt$_4$][Pt^{II}Br$_3$(CO)] (**1**) are similar to those reported for [NEt$_4$][Pt^{IV}Br$_3$H$_2$(CO)]. It might be argued that the small size of the hydride ligands and their presumed *trans* arrangement in the latter compound could be responsible for these negligible structural differences. However, the presence of hydride ligands can be ruled out on the basis of spectroscopic data (see above). Thus, it can be concluded that the
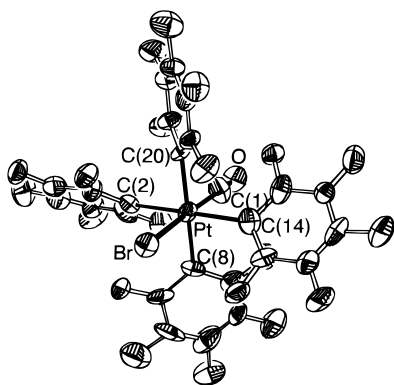
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Figure 2. Thermal ellipsoid diagram of the anion of **2**.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for the Anion of 2

Pt−C(1)	1.91(3)	Pt−C(14)	2.13(2)
Pt−Br	2.474(4)	Pt−C(20)	2.11(2)
Pt−C(2)	2.10(2)	C(1)−O	1.13(3)
Pt−C(8)	2.09(2)		
Pt−C(1)−O	174(2)	C(8)−Pt−C(14)	89.7(8)
C(1)−Pt−C(2)	93(1)	C(8)−Pt−Br	89.1(6)
C(1)−Pt−C(8)	89.7(9)	C(14)−Pt−C(20)	91.3(8)
C(1)−Pt−C(14)	86(1)	C(14)−Pt−Br	91.0(7)
C(1)−Pt−C(20)	90.1(9)	C(20)−Pt−Br	91.1(6)
C(2)−Pt−C(8)	89.8(8)	C(1)−Pt−Br	177.0(8)
C(2)−Pt−C(20)	89.1(7)	C(2)−Pt−C(14)	179.5(6)
C(2)−Pt−Br	89.1(6)	C(8)−Pt−C(20)	178.9(7)

complex originally formulated as $[NEt_4][Pt^{IV}Br_3H_2(CO)]$ is, in fact, the Pt(II) carbonyl compound $[NEt_4][Pt^{II}Br_3(CO)]$ (**1**). Considering the reported $\nu(C\equiv O)$ and $\nu(Pt-H)$ values (Table 1), we suggest that all the anions $[Pt^{IV}X_3H_2(CO)]^-$ (X = Cl, Br or I) should be formulated as $[Pt^{II}X_3(CO)]^-$. As a result, the nature of the parent, neutral, "five-coordinate" species "$Pt^{IV}X_2H_2(CO)$" becomes more than dubious. Once again, the low $\nu(CO)$ values reported for these species are inconsistent with the high oxidation state suggested for the metal center (Table 1).[32] The same inconsistency is observed in other neutral or even cationic Pt(IV) carbonyl derivatives reported, namely the compounds *fac*-$[PtIMe_3(SMe_2)(CO)]$ (not isolated, $\nu(C\equiv O)$ = 2090 cm^{-1})[16a] and $[PtClIMe\{CH(py)Et\}(py)(CO)]^+Cl^-$ (isolated, $\nu(C\equiv O)$ = 2060 cm^{-1}),[16b] the formulation of which should, in our opinion, be reconsidered. Higher $\nu(CO)$ values have, in turn, been reported for $[PtMe_3\{(C_3H_3N_2)_2BH_2\}(CO)]$, which readily loses the CO molecule (not isolated, $\nu(C\equiv O)$ = 2125 cm^{-1}),[13b] and for $[NH_2{}^iPr_2][PtCl_5(CO)]$ (isolated, $\nu(C\equiv O)$ = 2191 cm^{-1}).[12]

Considering its very high $\nu(CO)$ value, complex $[NH_2{}^iPr_2][PtCl_5(CO)]$ appears to be the most firmly established example of an isolated carbonyl derivative of Pt(IV). It has been obtained by oxidative addition of Cl_2 to the substrate $[NH_2{}^iPr_2][Pt^{II}Cl_3(CO)]$ in thionyl chloride solution.[12] The new complex $[NBu_4][Pt^{IV}(C_6F_5)_4Br(CO)]$ (**2**) has been prepared following a related synthetic procedure: oxidative addition of Br_2 to the Pt(II) substrate $[NBu_4]_2[Pt(C_6F_5)_4]$ followed by halide extraction with $AgClO_4$ in the presence of CO. The IR spectrum of **2** shows a sharp $\nu(CO)$ absorption at 2166 cm^{-1}. Given that this value is higher than that observed for free CO ($\nu(C\equiv O)$ = 2143 cm^{-1}),[33] it follows that the CO molecule in **2** is acting mainly as a σ-donor ligand, as expected for carbonyl complexes of Pt(IV). The crystal structure of **2** was determined by X-ray diffraction methods. An ellipsoid drawing of the anion [*trans*-$Pt^{IV}(C_6F_5)_4Br(CO)]^-$ appears in Figure 2. Selected bond distances and angles are given in Table 4. The Pt(IV) center is in the usual octahedral environment with the Br^- and CO ligands located in *trans* positions. The Pt−Br distance (2.474(4) Å) is approximately the mean value observed in anionic six-coordinate Pt(IV) complexes containing terminal Pt−Br bonds (2.47 Å).[34] The

Pt−CO bond in **2** (Pt^{IV}−C(1) 1.92(3) Å) is appreciably longer than that observed in **1** (Pt^{II}−C(1) 1.830(10) Å). This elongation is consistent with the expected decrease in the π-back contribution of the Pt−CO bond on going from Pt(II) to Pt(IV). The C(1)−O distance in **2** (1.13-(3) Å) is in turn very similar to that found in **1** (1.159-(12) Å), which once again evidences the well-known low sensitivity of the C−O distance to variations in multiple bond order.[35] The PtCO unit is almost linear (Pt−C(1)−O 174(2)°), and the Pt−C_6F_5 distances are similar to those found in other six-coordinate pentafluorophenyl derivatives of Pt(IV).[36]

Metal carbonyl complexes in which the CO molecule acts mainly as a σ-donor ligand are known to readily undergo substitution reactions, and thus, only by the careful use of very poor nucleophilic anions in superacidic conditions have Aubke and co-workers been able to prepare and isolate an interesting series of nonclassical metal carbonyl derivatives.[8,9] Complex **2** is reasonably stable at room temperature in the solid state and in solution. The global negative charge on the complex as well as its saturated character (both electronic and coordinative) can contribute to the stability of **2**. The anion of **2** in solution has a remarkably static behavior, as revealed by its ^{19}F NMR spectrum which shows a single resonance for the *para*-F atoms (δ = −160.2 ppm) but two signals for each the *ortho*-F (δ = −110.0 and −115.3 ppm) and the *meta*-F atoms (δ = −163.1 and −164.2 ppm), thus implying that the rotation of the C_6F_5 rings around the Pt−C bond is restricted at room temperature. Given that at least in the solid state (Figure 2) all four C_6F_5 groups are arranged helically around the Br−Pt−CO axis (mean dihedral angle = 45°), it can be considered that they have a protective effect on the Pt-bound CO ligand.

Supporting Information Available: Tables of crystallographic data, atomic parameters, anisotropic displacement coefficients, and complete bond distances and angles for **1** and **2** (12 pages). Ordering information is given on any current masthead page.

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