$[\{Pt(CO)_3\}_2]^{2+}$: The First Homoleptic, Dinuclear, Cationic Platinum(I) Carbonyl Complex Formed in Concentrated Sulfuric Acid[**]

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In the last ten years there has been a rapid development in the preparation and structural characterization of homoleptic metal carbonyl cations of late transition metals, following the discovery that they can be prepared in superacid media. This area has recently been reviewed[1] and, apart from the CO-bridged dinuclear palladium(I) complex $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$[2a] and the unstable dinuclear mercury(I) carbonyl cation $[Hg_2(CO)_2]^{2+}$,[2b] all the complexes are monomeric with values of $\tilde{\nu}$(CO) significantly higher than 2143 cm^{-1}, the value for free CO.[3] In the 1970s the homoleptic, anionic platinum carbonyl clusters $[Pt_3(CO)_6]_n^{2-}$ ($n = 1-6$, ≈ 10)[4a] and $[Pt_{19}(CO)_{12}(\mu_2\text{-}CO)_{10}]^{4-}$,[4b] in which the Pt atoms are bridged by CO ligands, were reported. In 1993 the first homoleptic carbonyl complex of platinum(II), $[Pt(CO)_4][Pt(SO_3F)_6]$, was isolated from the incomplete reduction of $Pt(SO_3F)_4$ with CO at 25 °C.[5a] Subsequently, the complex $[Pt(CO)_4][Sb_2F_{11}]_2$ was prepared by solvolysis of *cis*-$[Pt(CO)_2(SO_3F)_2]$, which is formed by complete reduction of $Pt(SO_3F)_4$ with CO[5b] in liquid SbF_5.[5c] Both the vibrational and NMR spectra of $[Pt(CO)_4]^{2+}$ and *cis*-$[Pt(CO)_2(SO_3F)_2]$ are entirely consistent with a square-planar coordination due to Pt adopting a +2 oxidation state.

We now report on the preparation and spectroscopic characterization of the first homoleptic, dinuclear, cationic platinum(I) carbonyl complex, $[\{Pt(CO)_3\}_2]^{2+}$ (**1**), in which the Pt atoms are bound by a direct Pt–Pt bond. This unusual complex is formed as a result of the reductive carbonylation of PtO_2 by CO in concentrated sulfuric acid at room temperature and atmospheric pressure. The reaction takes about two weeks to complete [Eq. (1)], producing a colorless solution of **1**. Prolonged (ca. 1 d) evacuation of a solution of **1** in concentrated H_2SO_4 results in disproportionation and the exclusive formation of *cis*-$[Pt(CO)_2]^{2+}$(solv) (**2**), but slow reformation of **1** occurs on addition of CO [Eq. (2)]. Both **1** and **2** are extremely sensitive to moisture, exposure results in immediate decomposition to platinum metal.

$$Pt^{IV}O_2 + CO \xrightarrow[\text{RT, 1 atm}]{\text{conc. } H_2SO_4} \underset{\mathbf{1}}{[\{Pt^{I}(CO)_3\}_2]^{2+}} \quad (1)$$

$$\mathbf{1} \underset{+4CO\,/\,\text{conc. } H_2SO_4}{\overset{-4CO\,/\,\text{conc. } H_2SO_4}{\rightleftharpoons}} \underset{\mathbf{2}}{cis\text{-}[Pt^{II}(CO)_2]^{2+}(\text{solv})} + Pt^0 \quad (2)$$

The formulation of **1** as a dimer is shown from both ^{13}C and ^{195}Pt NMR studies at natural abundance and 99 % ^{13}CO enrichment (Table 1). According to NMR simulations the observed spectra are in agreement with the presence of a T-shaped $Pt(CO)_3$ group and the presence of ^{195}Pt–$^{195}Pt'$ spin–spin coupling (550.9 Hz).

Furthermore, in the Raman spectrum of **1**, there is clear evidence for a very strong, sharp band due to $\tilde{\nu}$(Pt–Pt) at 165 cm^{-1}, which is strongly polarized ($\rho \approx 0.25$). An EXAFS study on **1** shows the presence of a Pt–Pt bond of 2.674 Å, which is approximately 0.1 Å shorter than the Pt–Pt distance in Pt foil.[6] IR and Raman results of **1** (Table 1) are consistent with a structure of D_{2d} symmetry (Figure 1), with only terminal CO groups and a direct Pt–Pt bond. According to calculations at the B3LYP level the conformation adopted by this molecule has a dihedral angle of exactly 90°.[6] This structure is related to the structure of $[\{PtCl_2(CO)\}_2]^{2-}$ which contains two slightly distorted T-shaped $PtCl_2$(CO)

Table 1. Spectroscopic properties of **1**, **2**, and related complexes.

Compound	$\tilde{\nu}(CO)_{IR}$ [cm^{-1}]	$\tilde{\nu}(CO)_{Raman}$ [cm^{-1}]	$\delta(^{13}C)$	$\delta(^{195}Pt)$	^1J(Pt,C) [Hz]	Ref.
$[\{Pt(CO)_3\}_2]^{2+}$ **1**[a]	2195, 2186, 2174	2233, 2209, 2194, 2173[b]	158.7,[c] 166.3[d]	– 211.0	1595.7,[c] 1281.5[d,e]	[f]
cis-$[Pt(CO)_2]^{2+}$(solv) **2**[a]	2218, 2182	2219, 2182	133.7	957.9	1907.3	[f]
cis-$[Pt(CO)_2(SO_3F)_2]$[g]	2219, 2185	2218, 2181	131		2011	[5b]
cis-$[Pt(CO)_2Cl_2]$[h]	2178, 2137	2172, 2131	151.6		1576	[10]
$[Pt(CO)_4][Sb_2F_{11}]_2$[g]	2244	2289, 2267	137		1550	[5c]

[a] In conc. H_2SO_4. [b] $\tilde{\nu}(Pt\text{–}Pt)_{Raman} = 165\ cm^{-1}$. [c] For $^{13}C_A$; see Figure 1 for labeling scheme. [d] For $^{13}C_B$. [e] Other coupling constants [Hz]: $^1J(Pt,Pt') = 550.9$, $^2J(Pt,C_A) = -26.2$, $^2J(Pt,C_B) = 199.6$, $^2J(C_A,C_B) = 0$, $^3J(C_A,C_A) = 0$, $^3J(C_A,C_B) = 0$, $^3J(C_B,C_B) = 19.8$. [f] This paper. [g] In the solid state. [h] Spectroscopic data listed were obtained in benzene.

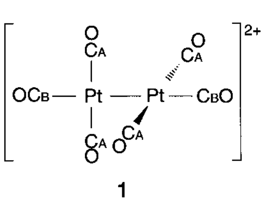

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Figure 1. Schematic structure of $[\{Pt(CO)_3\}_2]^{2+}$ (**1**), along with the labeling scheme for the carbonyl groups.

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groups with a dihedral angle of 60° between the two planes and in which both CO groups are *cisoid* (length of the Pt–Pt bond 2.584 Å).[7a] Other related, crystallographically characterized dinuclear platinum carbonyl species include $[\{PtCl(CO)(PtBu_2Ph)\}_2]$[7b] and $[\{Pt(C_6F_5)(CO)(PPh_3)\}_2]$,[7c] which have dihedral angles of 70.1° and 78.6°, and Pt–Pt distances of 2.628 and 2.599(Å), respectively. Preliminary reports have also appeared for $[\{PtCl(CO)(PPh_3)\}_2]$[8] and, in all cases, the carbonyl groups are *cis* and the two phosphanes are *trans* to the Pt–Pt bond.

It has been shown that there is no correlation of *d*(Pt–Pt) with $^1J(Pt,Pt')$ in closely related dinuclear platinum complexes.[8] It is worth noting that $^1J(Pt,Pt')$ for **1** is 550.9 Hz, while the values for $[\{PtCl_2(CO)\}_2]^{2-}$ (5250 Hz)[9] and $[\{PtCl(CO)(PPh_3)\}_2]$ (760 Hz)[8] are widely different, although other related coupling constants are similar (see Table 1 and refs. [8, 9]).

Prolonged evacuation of **1** results in disproportionation and formation of **2** through loss of CO [see Eq. (2)]. In this case, ^{13}C and ^{195}Pt NMR measurements on unenriched and 99% ^{13}CO-enriched **2** show that there are two magnetically equivalent carbonyl groups per platinum with no ^{195}Pt–^{195}Pt coupling; **2** is thus a monomer. We presently favor a square-planar platinum(II) center with two CO ligands in a *cis* configuration, consistent with both IR and Raman measurements; the CO stretching frequencies are close to those for *cis*-$[Pt(CO)_2(SO_3F)_2]$,[5b] but higher than those for *cis*-$[Pt(CO)_2Cl_2]$.[10] It is difficult to be sure whether the other two coordination sites on platinum are occupied by a bidentate SO_4^{2-} or by two monodentate SO_4^{2-}/HSO_4^- groups since it is impossible to obtain any useful IR or Raman data in the sulfato region. However, when **1** is in concentrated H_2SO_4, it seems more probable that the other two sites are occupied by monodentate HSO_4^- groups as recently found for silver(I).[11]

The discovery of **1** suggests that homoleptic cationic carbonyl complexes of late transition metals in low oxidation states can be formed in media which are less acidic than the superacids that have been used previously. We found that this unusual dinuclear platinum carbonyl complex, **1**, exhibits high catalytic activity for the carbonylation of olefins;[12] future studies will investigate the detailed reaction mechanism of this catalytic activity and attempts will be made to obtain **1** as a crystalline salt.

Experimental Section

Standard canula transfer techniques were used for all sample manipulations. NMR spectra were recorded in D_2SO_4 at room temperature on a Bruker AMX 200. The ^{13}C chemical shifts were referenced to external tetramethylsilane (TMS), and ^{195}Pt chemical shifts were referenced to 42.8 MHz at such a magnetic field that the protons in external TMS resonate at exactly 200 MHz. NMR simulations were carried out using gNMR 4.1 (Cherwell Scientific, Oxford, UK). Infrared spectra were obtained on thin films between two silicon discs on a JASCO FT/IR-230 spectrometer. Raman spectra were recorded on a Nicolet FT-Raman 960 spectrometer.

1: PtO_2 (2 mmol) in 96% H_2SO_4 (10 mL) was vigorously stirred for 2 weeks under ^{12}CO at constant pressure (1 atm), whereupon the dark colloidal suspension became colorless. The resulting solution is very moisture sensitive. Complex **1** with 99% ^{13}CO was prepared similarly.

2: The IR spectrum of **1** in 96% H_2SO_4 was monitored with time under evacuation (0.001 Torr). When the band for **1** (2174 cm^{-1} for ^{12}CO and 2126 cm^{-1} for ^{13}CO) had disappeared (ca. 1 d), nitrogen was admitted to the solution, which contained only **2** and a black colloidal precipitate of Pt metal. The solution of **2** was transferred under nitrogen by canula and used for all the spectroscopic measurements. This solution is indefinitely stable under a nitrogen atmosphere.

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Enantioselective Total Synthesis of Epothilone A Using Multifunctional Asymmetric Catalyses**

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Epothilones (see Scheme 1 for epothilones A (**1**) and B (**2**)) show potent antitumor activity by binding and stabilizing microtubules in the same way as taxol, and they are promising drug candidates. Epothilones A and B were isolated from the

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