1582 *Organometallics* **1994,** *13,* 1582-1585

Mixed Olefin-Carbonyl Complexes of Platinum(II)

Daniela Belli Dell'Amico, Fausto Calderazzo,* and Nicola Pasqualetti

Sezione di Chimica Inorganica, Dipartimento di Chimica e Chimica Industriale,
Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy

Cäcilia Maichle-Mössmer, Joachim Strähle,* and Klaus Wurst

Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18,
D-72076 Tübingen, Federal Republic of Germany

Received February 10, 1993[⊗]

The reaction of *cis*-$PtCl_2(CO)_2$ with cycloheptene in dichloromethane yielded *cis*-$PtCl_2(CO)(C_7H_{12})$ (1), characterized by X-ray diffraction methods. The dimeric bromide $Pt_2Br_4(CO)_2$ and cycloheptene in CH_2Cl_2 solution after workup and precipitation with heptane yielded a mixture of two solids, one of which, 2, was found crystallographically to be $Pt_2Br_4(C_7H_{12})_2 \cdot 2$[*cis*-$PtBr_2(CO)(C_7H_{12})$], an infrequent case of cocrystallization of two different molecules. Compound 1 crystallizes in the orthorhombic space group *Pbcm* with $a = 10.679(3)$ Å, $b = 13.533(1)$ Å, $c = 7.459(4)$ Å, and $V = 1078(1)$ Å^3 for $Z = 4$. Least-squares refinement of 1083 observed unique reflections gave $R = 0.042$ ($R_w = 0.048$). Compound 2 crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.106(3)$ Å, $b = 11.872(2)$ Å, $c = 12.908(7)$ Å, $\alpha = 72.79(3)°$, $\beta = 84.15(2)°$, $\gamma = 81.96(2)°$, and $V = 1078.1$ Å^3 for $Z = 2$. Least-squares refinement of 3637 observed reflections gave $R = 0.047$ ($R_w = 0.056$).

Introduction

In a recent paper some of us[1] reported that mixed olefin-carbonyl complexes of platinum(II) of formula $PtX_2(CO)(olefin)$ (X = Cl, Br; olefin = C_2H_4, C_3H_6, cyclopentene, cyclohexene) are best prepared by the reaction of the carbonyl dimer $Pt_2X_4(CO)_2$ with the stoichiometric amount of the olefin. On the basis of spectroscopic methods in solution, the compounds were suggested to be monomeric with a *cis* arrangement of the ligands around square-planar platinum(II). We now report the isolation of the cycloheptene derivative *cis*-$PtCl_2(CO)(C_7H_{12})$, which has been studied by X-ray diffractometric methods, thus confirming the earlier structural assignment.[1] Furthermore, the bromide derivative *trans*-$Pt_2Br_4(CO)_2$ was shown to react with cycloheptene, yielding two types of single crystals; we could solve one of the structures, which turned out to be formed by molecules of the monomer *cis*-$PtBr_2(CO)(C_7H_{12})$ and of the dimer $Pt_2Br_4(C_7H_{12})_2$.

The relative affinity of olefins and CO for late-transition-metal cations is an important problem in connection with the palladium-catalyzed copolymerization of CO and olefins.[2] Earlier work from these laboratories had shown that AuCl(olefin) was slightly favored with respect to AuCl(CO) at atmospheric pressure of CO.[3] In the case of square-planar palladium(II) or platinum(II), two coordination sites are available for the simultaneous coordination of CO and olefin.

Experimental Section

All the operations reported in this paper were carried out under an atmosphere of dinitrogen. Solvents were dried by conventional methods, and cycloheptene was distilled prior to use. *cis*-$PtCl_2(CO)_2$ was prepared by carbonylation of "hexachloroplatinic acid" in thionyl chloride[4] or by chlorination of $PtI_2(CO)_2$ (*cis* and *trans* mixture) with SO_2Cl_2;[5] *trans*-$Pt_2Br_4(CO)_2$[6] was prepared according to literature methods. The IR spectra in the 4000-400-cm^{-1} region were measured with a Perkin-Elmer 1725/X instrument on KBr pellet, unless otherwise specified.

Synthesis and Characterization of *cis*-$PtCl_2(CO)(C_7H_{12})$ (1). The chloro-carbonyl derivative *cis*-$PtCl_2(CO)_2$ (0.500 g, 1.55 mmol) was dissolved in 25 mL of CH_2Cl_2; 0.2 mL (0.16 g, 1.71 mmol) of cycloheptene was added to the solution, which was then stirred for 20 min at room temperature under intermittent evacuation. A complete conversion of the chlorocarbonyl (ν_{CO} 2177 and 2133 cm^{-1}) to the olefin-carbonyl derivative (ν_{CO} 2120 cm^{-1}) occurred. Transparent needles of 1 precipitated out by addition of hexane. IR spectrum (cm^{-1}): 2121, 1462 (w), 1377 (w), 530 (w). IR in toluene solution (cm^{-1}): ν_{CO} 2111.

Synthesis of [$PtBr_2(C_7H_{12})$]$_2$·2[*cis*-$PtBr_2(CO)(C_7H_{12})$] (2). The brown-yellow dimeric bromo-carbonyl complex $Pt_2Br_4(CO)_2$ (0.23 g, 0.38 mmol) was dissolved in 20 mL of toluene (ν_{CO} 2120 cm^{-1}) and treated with 0.4 mL (0.32 g, 3.42 mmol) of cycloheptene. The solution, which had immediately turned pale yellow (ν_{CO} 2105 cm^{-1}), was almost completely evaporated, and the residue was then redissolved in 20 mL of CH_2Cl_2 (ν_{CO} 2114 cm^{-1}). By addition of heptane, a solid (ν_{CO} 2118 (s), 2100 (sh) cm^{-1}) containing two types of crystals was obtained from the dichloromethane solution. Under the microscope it was possible to separate[7] the colorless needles (IR of selected crystals: ν_{CO} 2118 cm^{-1}) from the orange crystals of 2 (IR of selected crystals: ν_{CO} 2100 cm^{-1}), which were subsequently subjected to the X-ray diffraction experiment (*vide infra*).

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1994.

[1] Alper, H.; Huang, Y.; Belli Dell'Amico, D.; Calderazzo, F.; Pasqualetti, N.; Veracini, C. A. *Organometallics* **1991**, *10*, 1665.

[2] (a) Tsuji, J.; Morikawa, M.; Kiji, J. *J. Am. Chem. Soc.* **1969**, *86*, 4851. (b) Lai, T.-W.; Sen, A. *Organometallics* **1984**, *3*, 866. (c) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235. (d) Wang, P. K.; van Doorn, J. A.; Drent, E.; Sudmeijer, O.; Stil, H. A. *Ind. Eng. Chem. Res.* **1993**, *32*, 986.

[3] Belli Dell'Amico, D.; Calderazzo, F.; Dantona, R.; Strähle, J.; Weiss, H. *Organometallics* **1987**, *6*, 1207.

[4] Belli Dell'Amico, D.; Calderazzo, F. *Gazz. Chim. Ital.* **1979**, *109*, 99.

[5] Pasqualetti, N. Ph.D. Thesis, Università di Pisa, 1988.

[6] (a) Andreini, B. P.; Belli Dell'Amico, D.; Calderazzo, F.; Pelizzi, G.; Segre, A. *J. Organomet. Chem.* **1988**, *354*, 357.

[7] We could carry out a diffractometric experiment on one of the colorless crystals of the main species, but we were not able to solve the structure completely. We found rather large cell constants ($a = 7.38$ Å, $b = 11.26$ Å, $c = 26.19$ Å at -50 °C) in the orthorhombic space group *Pna2₁* or *Pnam* and proceeded in the refinement to an R value of 0.096; also in this case, the *cis*-$PtBr_2(CO)(C_7H_{12})$ unit was identified with certainty. For a second unit (containing a disordered Pt atom position, a cycloheptene moiety, and a bromine atom), a chemically significant solution could not be found.

0276-7333/94/2313-1582$04.50/0

Table 1. Experimental Details of the X-ray Diffraction Study of *cis*-$PtCl_2(CO)(C_7H_{12})$ (1) and $Pt_2Br_4(C_7H_{12})_2 \cdot 2[$*cis*-$PtBr_2(CO)(C_7H_{12})]$ (2)

	1	2
formula	$C_8H_{12}Cl_2OPt$	$C_{15}H_{24}Br_4OPt_2$
fw	390.18	930.20
$F(000)$	720	836
form and color	colorless needles	orange plates
dimens, mm	0.05 × 0.05 × 0.2	0.1 × 0.1 × 0.05
d_{calcd}, g cm^{-3}	2.404	3.030
space group	*Pbcm*; orthorhombic	$P\bar{1}$; triclinic
a, Å	10.679(3)	7.106(3)
b, Å	13.533(1)	11.871(2)
c, Å	7.459(4)	12.908(7)
α, deg	90	72.78(3)
β, deg	90	84.15(2)
γ, deg	90	81.96(2)
Z	4	2
V, Å^3	1078(1)	1027.8(7)
scan mode	ω/θ	ω/θ
μ(Mo Kα), cm^{-1}	136.09	216.17
correction method	DIFABS[6]	DIFABS[6]
min, max, and av cor	0.9247, 1.1277, 1.0013	0.7766; 1.4248; 1.0100
hkl interval	0–10; 0–15; –19 to +19	0–9; –16 to +16; –18 to +18
std rflns	(–1,5,4), (008), (019)	(–1,4,0), (150), (040)
intens control	every 1 h, no loss	every 1 h, no loss
no. of measd intens	3515; $3° < \theta < 30°$	6349; $3° < \theta < 30°$
no. of obsd intens	1083	3637
method of soln	direct methods[8]	Patterson synthesis[8]
weighting scheme	$1/\sigma^2$	$1/\sigma^2$
no. of refined params	65	200
R^a	0.042	0.047
$R_w{}^b$	0.048	0.056
max (Δ/σ)	0.00	0.03
residual density, e/Å^3	2.1	1.6
secondary extinctn coeff[10]	3.14×10^{-9}	3.64×10^{-8}

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum F_o{}^2]^{1/2}$, with $w = 1$.

X-ray Data Collection, Solution, and Refinement of the Crystal Structures. All X-ray experiments were carried out with an automated Enraf-Nonius CAD4 diffractometer using monochromated Mo Kα radiation (λ = 0.710 69 Å).

***cis*-$PtCl_2(CO)(C_7H_{12})$ (1).** A colorless, transparent crystal of 1 with approximate dimensions (mm) 0.05 × 0.05 × 0.2 was mounted on a glass rod and used for the X-ray diffraction experiment at –50 °C. The cell dimensions (see Table 1) were refined with 25 precisely centered reflections in the range $11.44° < \theta < 14.21°$. With the ω/θ scan mode in a $3° < \theta < 30°$ angular region, 3515 intensities were collected, from which 2069 independent reflections with $I > 3\sigma(I)$ were used in the calculation. From the Laue symmetry *mmm* and the zonal extinctions 0*kl* ($k = 2n$) and *h*0*l* ($l = 2n$) the possible space groups were restricted to the orthorhombic ones $Pbc2_1$ (No. 29) and *Pbcm* (No. 57). With direct methods[8] (SHELX) a solution was found in the space group *Pbcm*. The refinement of all atoms with isotropic temperature factors gave R = 0.103; this value decreased to 0.057 after an absorption correction with the DIFABS method[9] and merging over the symmetry-related reflections. The anisotropic refinement of all atoms gave R = 0.049, and finally, after refinement of the secondary extinction coefficients[10] and calculation of the positions for the H atoms, the value R = 0.042 (R_w = 0.048) was obtained. Atomic coordinates are given in Table 2.

Table 2. Positional and Thermal Parameters for *cis*-$PtCl_2(CO)(C_7H_{12})$[a]

atom	x	y	z	B (Å^2)
Pt	0.69219(6)	0.29699(4)	0.250	2.142(9)
Cl(1)	0.8695(4)	0.2015(3)	0.250	2.80(7)
Cl(2)	0.5666(5)	0.1565(3)	0.250	3.44(9)
O(11)	0.449(1)	0.403(1)	0.250	4.5(3)
C(11)	0.544(2)	0.368(1)	0.250	2.9(3)
C(1)	0.809(1)	0.4199(8)	0.157(2)	2.5(2)
C(2)	0.749(1)	0.5029(8)	0.051(2)	3.0(3)
C(3)	0.828(2)	0.5984(9)	0.076(2)	4.1(3)
C(4)	0.796(2)	0.654(1)	0.250	3.4(4)
H(11)	0.8908	0.4291	0.2031	3.2*
H(21)	0.6646	0.5145	0.0906	3.8*
H(22)	0.7454	0.4857	–0.0741	3.8*
H(31)	0.8136	0.6415	–0.0232	5.1*
H(32)	0.9140	0.5802	0.0780	5.1*
H(41)	0.8485	0.7114	0.2591	4.2*

[a] Numbers in parentheses are estimated standard deviations in the least significant digit. Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 3. Positional and Thermal Parameters for $Pt_2Br_4(C_7H_{12})_2 \cdot 2[$*cis*-$PtBr_2(CO)(C_7H_{12})]$[a]

atom	x	y	z	B (Å^2)
Pt(1)	0.06360(9)	0.13615(5)	0.07977(5)	1.82(1)
Pt(2)	0.97894(8)	0.39691(5)	0.42085(5)	1.66(1)
Br(11)	0.2120(4)	–0.0651(2)	0.1248(2)	3.92(5)
Br(12)	–0.2090(3)	0.0796(2)	0.2085(2)	3.01(4)
Br(21)	0.8526(3)	0.4290(2)	0.5953(1)	2.51(3)
Br(22)	1.1317(3)	0.3837(2)	0.2496(1)	2.98(3)
O	–0.142(2)	0.380(1)	0.040(1)	3.9(3)
C(1)	–0.063(2)	0.291(1)	0.054(2)	2.7(4)
C(11)	0.246(2)	0.173(1)	–0.073(1)	2.0(3)
C(12)	0.343(2)	0.196(1)	0.007(1)	2.2(3)
C(13)	0.378(3)	0.321(1)	0.006(2)	2.6(4)
C(14)	0.514(3)	0.371(1)	–0.091(2)	2.7(4)
C(15)	0.412(3)	0.421(2)	–0.200(2)	2.9(4)
C(16)	0.341(3)	0.331(2)	–0.242(2)	3.4(4)
C(17)	0.170(3)	0.270(2)	–0.168(1)	2.9(4)
C(21)	0.760(2)	0.295(2)	0.403(2)	2.6(4)
C(22)	0.912(3)	0.216(1)	0.452(2)	2.6(3)
C(23)	0.889(2)	0.144(2)	0.572(1)	2.5(4)
C(24)	0.753(3)	0.048(1)	0.580(2)	2.8(4)
C(25)	0.542(3)	0.099(1)	0.587(1)	2.2(3)
C(26)	0.468(2)	0.196(2)	0.487(2)	3.2(4)
C(27)	0.567(3)	0.314(2)	0.462(2)	3.2(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

$Pt_2Br_4(C_7H_{12})_2 \cdot 2[$*cis*-$PtBr_2(CO)(C_7H_{12})]$ (2). The measurement on the crystals of 2 was performed at –70 °C; the cell parameters (see Table 1) were determined on the basis of 25 precisely measured reflections in the range $6.46° < \theta < 17.17°$. A total of 6349 intensities were collected in the $3° < \theta < 30°$ angular region, from which 3637 independent values with $I > 3\sigma(I)$ were used in the calculation. With a Patterson method, two distinct molecules were identified in the asymmetric unit. In one of the molecules the positional parameters for the platinum and two bromine atoms were assigned; in the other one, one platinum and one bromine atom were located (R = 0.214). In the following difference Fourier syntheses, a C_7 cyclic unit for both platinum atoms was identified (R = 0.127) and the structure of the asymmetric unit with chemically independent square-planar *cis*-$PtBr_2(CO)(C_7H_{12})$ and $^1/_2Pt_2Br_4(C_7H_{12})_2$ was established. The inversion center lies in the middle of the $Pt(\mu\text{-}Br)_2Pt$ moiety of the $Pt_2Br_4(C_7H_{12})_2$ dimer. An absorption correction[9] gave R = 0.062, and the insertion of anisotropic thermal parameters for all atoms decreased the R value to 0.048 (R_w = 0.057); the refinement of the secondary extinction coefficient[10] gave the final value R = 0.048 (R_w = 0.056). Atomic coordinates are given in Table 3.

Results and Discussion

The mixed carbonyl–cycloheptene complexes of platinum(II) have been prepared by reactions 1 and 2.

---

(8) Sheldrick, G. M. SHELX-86; Universität Göttingen, Göttingen, FRG, 1986.
(9) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(10) Zachariasen, W. H. *Acta Crystallogr.* **1963**, *16*, 1139.

$$cis\text{-}PtCl_2(CO)_2 + C_7H_{12} \rightleftarrows cis\text{-}PtCl_2(CO)(C_7H_{12}) + CO \quad (1)$$

$$trans\text{-}Pt_2Br_4(CO)_2 + 2C_7H_{12} \rightarrow 2\ cis\text{-}PtBr_2(CO)(C_7H_{12}) \quad (2)$$

Removal of CO was necessary in order to displace equilibrium 1 to the right. While compound 1 was the sole product of reaction 1, the mixed carbonyl–olefin derivative *cis*-PtBr$_2$(CO)(C$_7$H$_{12}$) was obtained in reaction 2 as the second component of the single crystals of 2, in a 2:1 molar ratio with *trans*-Pt$_2$Br$_4$(C$_7$H$_{12}$)$_2$. It is believed that the carbonyl–olefin bromide complex of eq 2 is formed *via* the intermediacy of *trans*-PtBr$_2$(CO)(C$_7$H$_{12}$), followed by isomerization to the thermodynamically stable *cis* isomer (see eqs 3 and 4). In an earlier paper,[11a] the carbonylation of *trans*-Pt$_2$X$_4$(CO)$_2$ (X = Cl, Br) was shown to occur through the intermediate formation of *trans*-PtX$_2$(CO)$_2$, which is unstable with respect to *cis*-PtX$_2$(CO)$_2$: a similar mechanism is therefore suggested for the olefin addition to the *trans*-dicarbonyl bromide dimer.

$$trans\text{-}Pt_2Br_4(CO)_2 + 2C_7H_{12} \rightarrow 2\ trans\text{-}PtBr_2(CO)(C_7H_{12}) \quad (3)$$

$$trans\text{-}PtBr_2(CO)(C_7H_{12}) \rightleftarrows cis\text{-}PtBr_2(CO)(C_7H_{12}) \quad (4)$$

trans-PtBr$_2$(CO)(C$_7$H$_{12}$) is also believed to be responsible for the formation of the *trans* dimer Pt$_2$Br$_4$(C$_7$H$_{12}$)$_2$ by loss of CO (see eq 5) as the second component of 2.

$$2\ trans\text{-}PtBr_2(CO)(C_7H_{12}) \rightleftarrows 2\ CO + Pt_2Br_4(C_7H_{12})_2 \quad (5)$$

The alternative possibility of CO dissociation from *cis*-PtBr$_2$(CO)(C$_7$H$_{12}$) (see eq 6) is less likely, by analogy with the observation that *cis*-PtX$_2$(CO)$_2$ species (X = Cl, Br) are substitionally inert.[6,11b]

$$2\ cis\text{-}PtBr_2(CO)(C_7H_{12}) \rightleftarrows 2CO + Pt_2Br_4(C_7H_{12})_2 \quad (6)$$

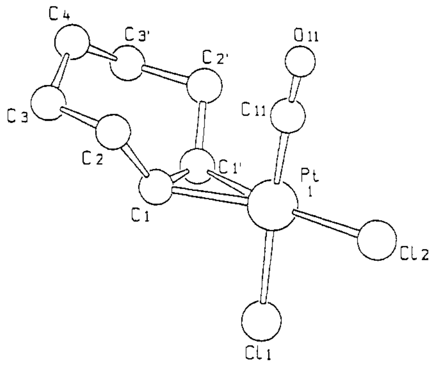

Figure 1. SCHAKAL view[12] of 1.

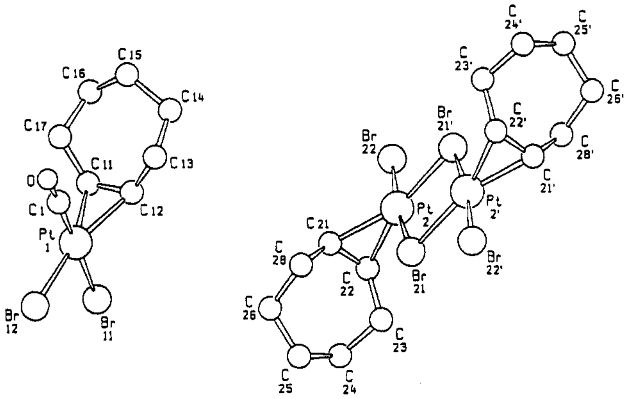

Figure 2. SCHAKAL view[12] of the complexes in 2.

Table 4. Bond Distances (Å) and Angles (deg) for *cis*-PtCl$_2$(CO)(C$_7$H$_{12}$)[a]

	Bond Distances		
Pt–Cl(1)	2.292(4)	C(1)–C(1′)	1.38(2)
Pt–Cl(2)	2.328(4)	C(1)–C(2)	1.52(2)
Pt–C(1)	2.20(1)	C(2)–C(3)	1.55(2)
Pt–C(11)	1.85(2)	C(3)–C(4)	1.53(2)
O(11)–C(11)	1.11(2)		
	Bond Angles		
Cl(1)–Pt–Cl(2)	90.9(2)	C(11)–Pt–C(1)	95.4(5)
Cl(1)–Pt–C(11)	176.8(5)	C(1)–Pt–C(1′)	36.8(5)
Cl(1)–Pt–C(1)	87.6(4)	C(1′)–C(1)–C(2)	122(2)
Cl(2)–Pt–C(11)	85.9(5)	C(1)–C(2)–C(3)	109(2)
Cl(2)–Pt–C(1)	161.6(3)	C(2)–C(3)–C(4)	113(1)
Cl(2)–Pt–C(1)	161.6(3)	C(3)–C(4)–C(3)	115(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

The structures of compounds 1 and 2, presented in this paper (see Figures 1 and 2), are a contribution to the series of structural data for the systems *cis*-PtX$_2$LL′ and (PtX$_2$L)$_2$, in which L and L′ are *trans*-labilizing donor ligands (see, for example, the compounds with L = L′ = styrene[13] and L = CO, L′ = PPh$_3$[14]). Both structures of the present study (see Tables 4 and 5) confirm the observation[14] that the halogen *trans* to the carbonyl group is closer to platinum than the halogen *trans* to the other neutral ligand: in 1, Cl(2)–Pt = 2.328(4) Å and Cl(1)–Pt = 2.292(4) Å, Δ = 0.036 Å; in 2, Br(12)–Pt = 2.453(2) Å and Br(11)–Pt = 2.400(2) Å, Δ = 0.053 Å. This is to be compared with Cl(1)–Pt(PPh$_3$) = 2.342(3) Å and Cl(2)–Pt(CO) = 2.277(3) Å (Δ = 0.065 Å) in *cis*-PtCl$_2$(CO)(PPh$_3$).[14] This should be taken as an indication of a weaker *trans* influence[15] of CO with respect to both olefins and tertiary phosphines. The C=C bond separation in the three Pt—(C$_7$H$_{12}$) environments, 1.38(2) Å in 1, 1.41(3) Å in *cis*-PtBr$_2$(CO)(C$_7$H$_{12}$), and 1.40(2) Å in Pt$_2$Br$_4$(C$_7$H$_{12}$)$_2$ in the asymmetric unit of 2, are in agreement with those found in *cis*-PtCl$_2$(styrene)$_2$ (1.382(9) and 1.398(9) Å[13]). Taking into account that a C=C double-bond length is *ca.* 1.34 Å and a C—C single bond is *ca.* 1.54 Å, our data for 1 and 2 suggest a rather modest π back-bonding contribution.

The platinum atom in 1 lies only 0.004 Å out of the plane formed by Cl(1), Cl(2), C(11), and the midpoint of the bond between C(1) and C(1′), as imposed by the mirror plane in the space group *Pbcm*. Also in 2 the platinum coordination geometry of the two components *cis*-PtBr$_2$(CO)(C$_7$H$_{12}$) and *trans*-Pt$_2$Br$_4$(C$_7$H$_{12}$)$_2$ is essentially

---

(11) (a) Belli Dell'Amico, D.; Calderazzo, F.; Veracini, C. A.; Zandonà, N. *Inorg. Chem.* **1984**, *23*, 3030. (b) Calderazzo, F. *J. Organomet. Chem.* **1990**, *400*, 303.

(12) Keller, E. SCHAKAL, Program zur graphischen Darstellung von Kristallstrukturen; Universität Freiburg, Freiburg, FRG, 1990.

(13) Albinati, A.; Caseri, W. R.; Pregosin, P. S. *Organometallics* **1987**, *6*, 788.

(14) Manojlović-Muir, L.; Muir, K. W.; Walker, R. *J. Organomet. Chem.* **1974**, *66*, C21.

(15) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1966.

Table 5. Bond Distances (Å) and Angles (deg) for $Pt_2Br_4(C_7H_{12})_2 \cdot 2[cis\text{-}PtBr_2(CO)(C_7H_{12})]^a$

	Bond Distances		
Pt(1)–Br(11)	2.400(2)	C(14)–C(15)	1.56(3)
Pt(1)–Br(12)	2.453(2)	C(15)–C(16)	1.51(3)
Pt(1)–C(1)	1.88(2)	C(16)–C(17)	1.58(3)
Pt(2)–Br(21)	2.454(2)	C(21)–C(22)	1.40(2)
Pt(2)–Br(22)	2.399(2)	C(21)–C(27)	1.52(3)
O–C(1)	1.10(2)	C(22)–C(23)	1.53(2)
C(11)–C(12)	1.41(3)	C(23)–C(24)	1.57(3)
C(11)–C(17)	1.51(2)	C(24)–C(25)	1.54(3)
C(12)–C(13)	1.54(3)	C(25)–C(26)	1.55(2)
C(13)–C(14)	1.54(2)	C(26)–C(27)	1.59(3)
Pt(1)–C(11)	2.21(2)	Pt(1)–C(12)	2.22(2)
Pt(2)–C(21)	2.18(2)	Pt(2)–C(22)	2.18(2)
	Bond Angles		
Br(11)–Pt(1)–Br(12)	91.48(7)	C(12)–C(11)–C(17)	122(2)
Br(11)–Pt(1)–C(1)	175.9(6)	C(11)–C(12)–C(13)	124(1)
Br(12)–Pt(1)–C(1)	84.7(5)	C(12)–C(13)–C(14)	108(2)
Br(21)–Pt(2)–Br(22)	172.41(8)	C(13)–C(14)–C(15)	113(2)
Br(11)–Pt(1)–C(11)	88.6(4)	C(14)–C(15)–C(16)	116(1)
Br(11)–Pt(1)–C(12)	89.0(5)	C(15)–C(16)–C(17)	113(2)
Br(12)–Pt(1)–C(11)	84.7(5)	C(11)–C(17)–C(16)	110(2)
Br(12)–Pt(1)–C(12)	162.5(6)	C(22)–C(21)–C(27)	123(2)
C(1)–Pt(1)–C(12)	94.3(7)	C(21)–C(22)–C(23)	120(2)
C(11)–Pt(1)–C(12)	37.1(7)	C(22)–C(23)–C(24)	107(2)
Br(21)–Pt(2)–C(21)	97.4(5)	C(23)–C(24)–C(25)	111(1)
Br(21)–Pt(2)–C(22)	98.4(5)	C(24)–C(25)–C(26)	117(1)
Br(22)–Pt(2)–C(21)	90.1(5)	C(25)–C(26)–C(27)	113(2)
Br(22)–Pt(2)–C(22)	88.3(5)	C(21)–C(27)–C(26)	108(2)
C(21)–Pt(2)–C(22)	37.7(6)	Pt(1)–C(1)–O	179(2)
C(1)–Pt(1)–C(11)	95.6(7)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

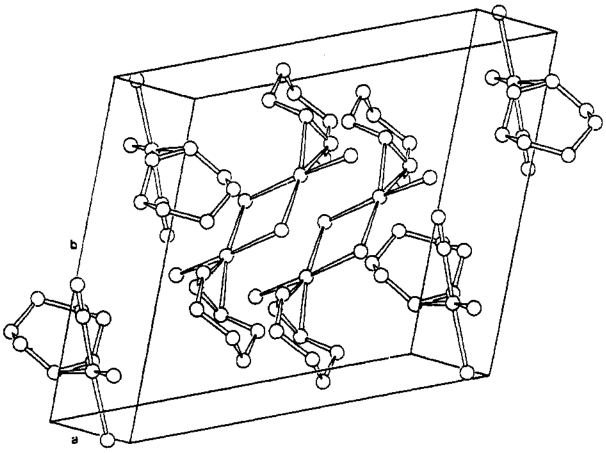

Figure 3. View of the molecular packing of the two different complexes of **2**.

planar and the distances between the platinum atom and the olefinic carbons are equal within the limits of the standard deviations: in *cis*-$PtBr_2(CO)(C_7H_{12})$, they are 2.20(2) and 2.22(2) Å; in the *trans*-$Pt_2Br_4(C_7H_{12})_2$ dimer, they are 2.16(2) and 2.17(2) Å.

The crystal packing of **2** (see Figure 3) appears to be mainly governed by van der Waals interactions.

The quite unusual feature of two different and independent molecules cocrystallizing in the same unit cell of **2** should also be noted. Such a feature is observed in a number of cases, when anions and cations are involved. For example, in a number of aurates, the cocrystallization of AuX_2^- and AuX_4^- or X_3^- and AuX_4^- was found: $Cs_2Au_2X_6$,[16,17] $Cs_3(AuBr_4)_2Br_3$,[18] $Rb_2Au_2Br_6$, $Rb_3Au_3Cl_8$,[19] and $Rb_2AgAu_3I_8$.[20] On the other hand, for neutral molecules, similar cases are also known, although they are rather rare. Gambarotta and co-workers[21] reported the X-ray crystal structure of the product obtained when a pyridine solution of $[Cr(TAA)(py)_2]\cdot py$ (TAA = tetramethyldibenzotetraaza[14]annulene) was layered with THF–hexane; one dinuclear $[Cr(TAA)]_2$ and two mononuclear pseudooctahedral $Cr(TAA)(py)_2$ molecules were found in the lattice, together with two molecules of THF and one disordered molecule of pyridine. Chisholm, Cotton, and co-workers[22] reported the diffractometric characterization of $2W_2(NMe_2)_6 \cdot W(NMe_2)_6$; in this case, the individual dinuclear and mononuclear components were also studied and the geometrical parameters were found to be in agreement with the structure containing both species. The structural characterization of $WCl_6 \cdot S_8$ is also relevant in this connection.[23] A case of cocrystallization of ionic and neutral complexes is represented by the structure of $[MoN(N_3)_2(terpy)][MoN(N_3)_4] \cdot MoN(N_3)_3(terpy)$.[24] In these structures, van der Waals interactions appear to be mainly responsible for the formation of the solid-state adducts.

On the other hand, as a distinct case from clathrates (*i.e.* solid-state structures including solvent molecules in their cavities), *cis*-$PtBr_2(CO)(C_7H_{12})$ and $^1/_2[PtBr_2(C_7H_{12})]_2$ have comparable steric requirements. While this article was in preparation, a paper appeared describing the crystal and molecular structure of $2[PtCl_2(9S3)] \cdot PtCl_2(1,5\text{-}C_8H_{12})$ (9S3 = trithiacyclononane).[25]

Acknowledgment. Financial support by the Consiglio Nazionale delle Ricerche (CNR), Rome, by the Ministero dell'Università e delle Ricerca Scientifica e Tecnologica (MURST), and by the Fonds der Chemischen Industrie is gratefully acknowledged.

Supplementary Material Available: Tables of general displacement parameters (*U*'s) for **1** and **2** (2 pages). Ordering information is given on any current masthead page.

OM930080Y

---

(16) Brauer, G.; Sleater, G. *J. Less-Common Met.* **1970**, *21*, 283.

(17) Ferrari, A.; Tani, M. E. *Gazz. Chim. Ital.* **1959**, *89*, 502.

(18) Lehnis, B.; Strähle, J. *Z. Naturforsch.* **1981**, *36B*, 1504.

(19) Strähle, J.; Gelinek, J.; Kölmel, M. *Z. Anorg. Allg. Chem.* **1979**, *456*, 241.

(20) Werner, W.; Strähle, J. *Z. Naturforsch.* **1979**, *34B*, 952.

(21) Hao, S.; Edema, J. H. H.; Gambarotta, S.; Bensimon, C. *Inorg. Chem.* **1992**, *31*, 2678.

(22) Chisholm, M. H.; Cotton, F. A.; Extine, M.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4477.

(23) Cotton, F. A.; Kibala, P. A.; Sandor, R. B. W. *Acta Crystallogr.* **1989**, *C45*, 1287.

(24) Beck, J.; Strähle, J. *Z. Anorg. Allg. Chem.* **1987**, *554*, 50.

(25) Bennett, M. A.; Felixberger, J. K.; Willis, A. C. *Gazz. Chim. Ital.* **1993**, *123*, 405.