DALTON COMMUNICATION

New preparative access to and the crystal and molecular structures of *cis*-[$PtCl_2(CO)_2$]

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cis-Dicarbonyldichloroplatinum(II) has been found to be the thermodynamically stable species arising from: (*a*) carbonylation of [NBu_4]$_2$[$PtCl_4$] in the presence of $AlCl_3$, (*b*) chlorination of [$PtI_2(CO)_2$]–[$Pt_2I_4(CO)_2$] with SO_2Cl_2 under CO and (*c*) carbonylation of $PtCl_2$; the crystal and molecular structures of *cis*-[$PtCl_2(CO)_2$] showed a short C–O distance [average 1.115(7) Å] and intermolecular Pt $\cdots$ Pt and C $\cdots$ Cl contacts of less than 3.4 Å.

The compound *cis*-dicarbonyldichloroplatinum(II) was reported by Schützenberger[1] in 1870, *i.e.* twenty years before the discovery of $Ni(CO)_4$, the first homoleptic metal carbonyl,[2] by L. Mond and co-workers. It was prepared in a two-stage process at 250 °C, first by converting platinum sponge with elemental chlorine to a platinum chloride which was then transformed by carbon monoxide into both *cis*-[$PtCl_2(CO)_2$] and [$Pt_2Cl_4(CO)_2$]. The mononuclear carbonyl compound (in benzene or toluene: ν_{CO}, 2170, 2128 cm^{-1}; ^{13}C NMR, δ 152.0, J_{Pt-C} 1569 Hz; ^{195}Pt NMR, δ −3879) can be more easily prepared[3,4] by the reductive carbonylation of anhydrous platinum(IV) chloride in thionyl chloride as solvent. The coupling constant J_{Pt-C} of halogeno–carbonyl complexes [$PtX_2(CO)_2$] decreases[4] in the sequence Cl > Br > I; this fact suggests that the strength of the Pt–C σ bond decreases from chloride to iodide through the bromide and that the Pt–CO bond is dominated by σ contribution.

The compound *cis*-[$PtCl_2(CO)_2$] has now been prepared in a number of more simple ways:† (*a*) carbonylation of a dichloromethane solution of [NBu_4]$_2$[$PtCl_4$] in the presence of aluminium trichloride as halide scavenger at room temperature and atmospheric pressure; (*b*) chlorination of [$PtI_2(CO)_2$]–[$Pt_2I_4(CO)_2$] using SO_2Cl_2 under CO followed by recrystallization of the crude product from toluene; (*c*) carbonylation of anhydrous $PtCl_2$ at room temperature and atmospheric pressure in chlorinated solvents. These new preparative procedures can be used to obtain further information about the nature of the Pt^{II}–CO bond.

The molecular structure of [$PtCl_2(CO)_2$] does not appear to have been studied before, presumably due to technical difficulties connected with the extreme sensitivity of the compound to moisture. On the other hand, the present views[5] about the predominant σ contribution in the M–CO bond of carbonyl derivatives of late transition metals in their usual oxidation states, combined with the still limited number of crystallographically established carbonyl derivatives in this area of the Periodic Table, prompted us to determine the crystal structure of the platinum(II) prototype. Single crystals of *cis*-[$PtCl_2(CO)_2$] were grown from heptane solution and studied by X-ray diffraction methods.‡ The compound shows the expected square-planar co-ordination around the 5d^8 platinum(II), as shown in Fig. 1.

The Pt–Cl bond distances of 2.2863(13) and 2.2972(13) Å are significantly *shorter* than those observed in other platinum(II) derivatives with terminal chloride groups. The Pt–Cl$_t$ (Cl$_t$ = terminal chloride) distance, mediated over 293 cases is 2.323(38) Å, the distance in the lower quartile being 2.297 Å (the bond length distribution is positively skewed, *i.e.* long values are more common than short ones).[9] This observation shows that in the present case a *trans* influence of the carbonyl ligands is not substantiated by the experimental data.

The Pt–CO distances of 1.901(5) and 1.893(5) Å are statistically[9] within the range of values observed in platinum–carbonyl complexes (1.853 Å, 29 cases, σ = 0.056, upper quartile 1.878 Å), but are among the *longest* hitherto observed.

The C–O distances of 1.110(7) and 1.121(6) Å are significantly *shorter* than the unweighted mean[9] of 1.145 Å (10 022 cases, the lower quartile being 1.132 Å). On the other hand, the distances observed for *cis*-[$PtCl_2(CO)_2$] are well within the range of values encountered in other neutral carbonyl derivatives of platinum(II). For example, in *cis*-[$PtCl_2(CO)(PPh_3)$][10] the C–O bond distance is 1.114(8) Å. In *cis*-[$Pd(SO_3F)_2(CO)_2$] the average C–O bond distance is 1.108(6) Å.[5m] Within the oxidation state II, a comparison can also be made with the nickel(II) carbonyl chloride [$NiCl_2(CO)(PMe_3)_2$], which has a C–O bond distance[11] of 1.127(4) Å, *i.e.* the same as that found in *cis*-[$PtCl_2(CO)_2$], within the experimental error.

The good quality of these data allows us to pinpoint three structural features for *cis*-[$PtCl_2(CO)_2$]: short Pt–Cl bonds,

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† (*a*) [NBu_4]$_2$[$PtCl_4$] (0.98 mmol) under a CO atmosphere in CH_2Cl_2 (30 cm^3) was stirred with aluminium trichloride (0.262 g, 1.96 mmol) for 12 h; after addition of heptane (50 cm^3) and cooling at −30 °C, *cis*-[$PtCl_2(CO)_2$] was recovered by filtration (92% yield). (*b*) A toluene solution of [$PtI_2(CO)_2$]–[$Pt_2I_4(CO)_2$] obtained by carbonylation, at room temperature and atmospheric pressure, of PtI_2 (13.40 g, 29.8 mmol) was treated with SO_2Cl_2 (12.0 cm^3) under CO. After work-up with toluene and heptane, the product was recovered in 90% yield. (*c*) Platinum(II) chloride (0.280 g, 1.05 mmol) suspended in CH_2Cl_2 (30 cm^3) underwent complete carbonylation (IR monitoring) over 2 d (84% yield).

‡ X-Ray structure determinations: data were collected both at room temperature and at 203 K on an Enraf-Nonius CAD4 automatic diffractometer and the diffraction patterns were measured on several crystals. The best results were obtained using a crystal of approximate dimensions 0.65 × 0.10 × 0.06 mm at 203 K with the ω–2θ scanning mode (3.0 < θ < 45.0°) and graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å); $C_2Cl_2O_2Pt$, $M = 322.0$, monoclinic, space group $P2_1/c$ (no. 14), $a = 7.1890(3)$, $b = 12.8594(7)$, $c = 6.6817(6)$ Å, $\beta = 105.024(7)°$, $U = 596.59(7)$ Å^3, $Z = 4$, $D_c = 3.585$ g cm^{-3}, μ(Mo-Kα) = 24.30 mm^{-1}, $F(000) = 560$; 19 614 reflections measured on the whole diffraction sphere, 5061 independent reflections ($R_{int} = 0.052$), 2526 unique reflections with $I > 1.0\ \sigma(I)$ used for further computations. The data were corrected for a slight isotropic decay of about 4%. An empirical absorption correction based on ψ scans was applied (maximum and minimum transmission 99.9, 61.6, average 82.69%, $R_{int} = 0.044$).[6] Structure solution was by conventional heavy-atom methods followed by Fourier-difference syntheses.[7] Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all atoms. Refinement converged with 65 parameters using a statistical weighting scheme $w = [\sigma^2(F_o)]^{\ 1}$ to values of $R = 0.021$ and $R' = 0.021$, $S = 0.482$. The room-temperature data collection [Ag-Kα radiation (λ = 0.560 87 Å), crystal size 0.9 × 0.4 × 0.2 mm, 7721 measured reflections, 1626 unique reflections with $I > 1.0\ \sigma(I)$ used for further computation; $R = 0.071$ and $R' = 0.055$, $S = 1.044$] gave the following bond distances (Å): Pt–Cl(1) 2.289(5), Pt–Cl(2) 2.296(5), Pt–C(1) 1.95(2), Pt–C(2) 1.95(2), C(1)–O(1) 1.08(2), C(2)–O(2) 1.08(2). Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/283.

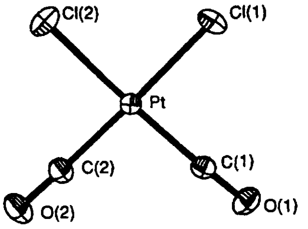

Fig. 1 PLATON[8] view of the molecular structure of *cis*-$[PtCl_2(CO)_2]$. Ellipsoids are scaled to 30% probability. Relevant bond distances (Å; values after translational-librational correction[8] in square brackets) and angles (°): Pt–Cl(1) 2.2863(13) [2.296(1)], Pt–Cl(2) 2.2972(13) [2.306(1)], Pt–C(1) 1.901(5) [1.909(5)], Pt–C(2) 1.893(5) [1.901(5)], C(1)–O(1) 1.110(7) [1.116(7)], C(2)–O(2) 1.121(6) [1.128(6)], Cl(1)–Pt–Cl(2) 90.88(6), Cl(1)–Pt–C(1) 86.5(2), Cl(1)–Pt–C(2) 178.4(2), Cl(2)–Pt–C(1) 177.4(2), Cl(2)–Pt–C(2) 87.7(2), C(1)–Pt–C(2) 94.9(2), Pt–C(1)–O(1) 177.9(5), Pt–C(2)–O(2) 178.4(5)

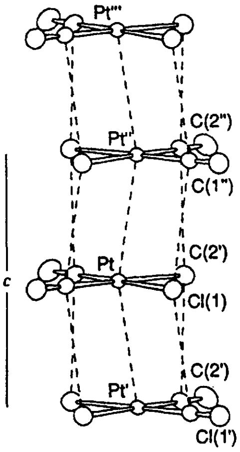

Fig. 2 View of molecular stacking in *cis*-$[PtCl_2(CO)_2]$. Relevant intermolecular distances (Å) and angles (°): Pt···Pt' 3.378(1), Cl(1)···C(1') 3.369(3), Cl(1)···C(1'') 3.437(4), Cl(2)···C(2') 3.333(4), Cl(2)···C(2'') 3.351(4); Pt'···Pt···Pt'' 162.90(1). Symmetry transformations: ' $x, \frac{1}{2}-y, z-\frac{1}{2}$, '' $x, \frac{1}{2}-y, z+\frac{1}{2}$, ''' $x, y, z+1$. Substantial overlapping occurs for each pair of *non-adjacent* platinum units with a periodicity of two

long Pt–C bonds and relatively short C–O bonds. These observations and the comparison of the metrical parameters with those of other carbonyl derivatives of late- (Pd^{II} or Pt^{II}) or post-transition elements {Au^I, Ag^I, Hg^{II}; for example[5k] in $[Ag(CO)_2]^+$ the average C–O distance is 1.08(6) Å} in their usual oxidation states lead us to confirm the earlier conclusions[5c–e] that binding of CO in these systems is mainly σ in nature. On the other hand, the real unconventional or atypical feature of these metal–carbonyl systems is that the strength of their M–CO bond does not appear to increase as the oxidation state decreases, as suggested, for example, by the low stability of the tetracarbonyls of palladium and platinum.

Work is now in progress aimed at estimating a value for the Pt^{II}–CO bond dissociation energy by using the thermodynamic parameters involved in the preparative methods (*a*) and (*c*). A recent estimate[12] of the Pd^{II}–CO bond dissociation energy gave a value of 104 ± 4 kJ mol^{-1}. The method of preparation (*c*) for *cis*-$[PtCl_2(CO)_2]$ confirms that CO successfully competes with bridging chlorides in the co-ordination sphere of platinum(II).

The crystal packing, which is shown in Fig. 2, consists of substantially planar molecules parallel to each other and stacked along the *c* axis. The platinum atoms form chains with Pt···Pt distances of 3.378(1) Å; the Pt'···Pt···Pt'' angle is less than 180° [162.90(1)°] in order apparently to optimize the C···Cl interplanar contacts.

This is a unique case of an uncharged platinum(II) system displaying rather short Pt···Pt contacts in the absence of possibly cooperating hydrogen bonds[13] or bridging ligands.[14] This study shows *cis*-$[PtCl_2(CO)_2]$ to be an example of supramolecular chemistry with apparently prevailing C···Cl interactions throughout the crystal. These findings should be compared with recent theoretical calculations on the hypothetical *cis*-$[PtCl_2(CO)_2]$ dimer.[15]

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