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Carbonyl complexes of noble metals with halide ligands

II *. Palladium(II): preparation of $Pd_2Br_4(CO)_2$ and $[PdI_3(CO)]^-$: crystal structures of $[Bu_4N][PdX_3(CO)]$ (X = Cl or Br)

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Abstract

The previously elusive $Pd_2Br_4(CO)_2$ has been isolated, mixed with $PdBr_2$, from the reaction of $PdBr_2$ with CO under pressure. A centrosymmetric structure is suggested for it on the basis of IR spectral data in solution. Attempts to prepare the corresponding iodo carbonyl complex of palladium(II) failed. The anion $[PdI_3(CO)]^-$ rapidly undergoes decarbonylation both in solution and in the solid state. The stabilities of the halocarbonyl complexes relative to those of the corresponding halides (PdX_2 or $Pd_2X_6{}^{2-}$) appear to decrease in the sequence $Cl > Br > I$. The crystal and molecular structures of the $[PdX_3(CO)]^-$ anions (X = Cl, Br) with $[N\text{-n-}Bu_4]^+$ as counter-cation have been determined by X-ray diffraction. Crystal data for $[N(n\text{-}C_4H_9)_4][PdCl_3(CO)]$: monoclinic; space group, $P2_1/n$; a 18.231(10); b 8.889(4); c 14.978(8) Å; β 104.88(2)°; U 2346(2) Å^3; $Z = 4$; D_c 1.368 g cm^{-3}; μ(Mo-K_α) 11.29 cm^{-1}; $R = 0.0397$. Crystal data for $[N(n\text{-}C_4H_9)_4][PdBr_3(CO)] \cdot C_2H_2Cl_4$: triclinic; space group, $P\bar{1}$; a 16.667(10); b 10.376(8); c 9.644(7) Å; α 74.27(3)°; β 75.12(3)°; γ 83.27(4)°; U 1549(2) Å^3; $Z = 2$; D_c 1.681 g cm^{-3}; μ(Mo-K_α) 47.84 cm^{-1}; $R = 0.0886$. In both anions, which are essentially planar, the Pd–X bond *trans* to the CO ligand is not significantly different in length from the other two Pd–X distances. The overall idealized symmetry of the $[N\text{-n-}Bu_4]^+$ cation

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* For part I see ref. 1.

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changes from D_{2d} to S_4 when the counter-anion is changed from $[PdCl_3(CO)]^-$ to $[PdBr_3(CO)]^-$.

Introduction

In the preceding paper [1], we described some new results on the behaviour of platinum(II) halocarbonyl complexes containing different halide ligands. For palladium, which is catalytically more active [2] than platinum in several reactions, there have been no systematic studies reported dealing with the effect of the nature of the halide ligand on the properties of the relevant compounds. Some years ago we prepared [3] $Pd_2Cl_4(CO)_2$, but the corresponding bromo and iodo derivatives were unknown at the beginning of this investigation. Of the anionic halo complexes, of formula $[PdX_3(CO)]^-$, the chloro and bromo compounds had been reported [4], but attempts to isolate $[PdI_3(CO)]^-$ were unsuccessful [4]. We therefore decided to study the palladium(II) system in some detail, with the aim of comparing the results with those for corresponding derivatives of platinum.

Experimental

The IR spectra were recorded with a Perkin–Elmer Model 283 grating spectrometer; each spectrum was calibrated with both CO and water vapour, and the wavenumbers are believed to be accurate to within ±1 cm^{-1}. Unless otherwise stated, all operations were carried out under prepurified nitrogen. Solvents were dried by standard.

Anhydrous palladium(II) bromide was prepared by heating under reflux a mixture of 6.0 g of palladium powder (56.39 mmol) (obtained by sodium formate reduction of $PdCl_4^{2-}$ in alkaline aqueous 10% $NaHCO_3$ [5]) with bromine (10 cm^3, 6 h). After an additional 15 h of stirring at room temperature, the remaining bromine was distilled off and the solid residue was dried in vacuo (67.6% yield). Satisfactory elemental analyses were obtained. The dimeric species $Pd_2Cl_4(CO)_2$ was prepared as previously described [6].

The $PdBr_2/CO$ system

(A) Metathetical reaction between $Pd_2Cl_4(CO)_2$ and HBr. The dimeric chloro carbonyl $Pd_2Cl_4(CO)_2$ (1.231 g, 3.0 mmol) was dissolved in toluene (50 cm^3) under nitrogen. The vessel was placed in a thermostatted bath at about −30 °C then evacuated. Dry HBr was introduced, and the mixture was stirred; after 3 h a red brown precipitate was noticed. The mixture was repeatedly treated with CO and dry HBr, and stirred for a total of 20 h after which the IR spectrum of the supernatant solution showed no bands from $Pt_2Cl_4(CO)_2$. The red brown solid ($PdBr_2$) was filtered off and dried in vacuo (1.58 g, a virtually quantitative yield). It gave a satisfactory analysis for Pd.

(B) Reaction of $PdBr_2$ with CO. Under atmospheric pressure, $PdBr_2$ was found to absorb only a small amount of CO (about 0.1 mmol per mmol of palladium) presumably because of chemisorption. At higher CO pressures the bromocarbonyl complex, $Pd_2Br_4(CO)_2$ was formed. A suspension of palladium(II) bromide (1.167

g, 4.38 mmol) in toluene (75 cm^3) was placed in a stainless-steel autoclave and carbon monoxide was introduced up to 70 atm pressure at room temperature. The mixture was stirred at 60 ° C for 8 h then at room temperature for 5 h. The gas was vented, the autoclave cooled to dry-ice temperature, and the mixture filtered to remove small amounts of suspended solids. The IR spectrum of the deep red solution, recorded as soon as possible, showed an intense band at 2148 cm^{-1} attributed to $Pd_2Br_4(CO)_2$. The solution, which had been maintained at dry-ice temperature, was diluted with n-heptane (100 cm^3). The orange bromocarbonyl that separates was filtered off on a pre-cooled filter and dried briefly in a stream of carbon monoxide. The solid progressively became brown during the drying; it was sealed under carbon monoxide in glass vials and kept at dry-ice temperature (0.36 g, 27.9% yield). The compound, analyzed for Pd, Br and CO (by reaction with PPh_3) gave the following results: Br, 53.9; CO, 7.1; Pd, 38.0%, corresponding to a 1.9/0.7/1.0 molar ratio.

The PdI_2/ CO system

(A) Attempted reaction between $Pd_2Cl_4(CO)_2$ and HI. The chloro carbonyl $Pd_2Cl_4(CO)_2$ (0.739 g, 1.80 mmol) was dissolved in toluene (25 cm^3) under nitrogen. The system was kept at ca. −30 ° C and dry HI was introduced. Rapid formation of a black solid was observed. Repeated treatments with HI and CO were carried out as the suspension was stirred for about 15 h. An IR spectrum of the supernatant solution showed that no soluble palladium carbonyl compounds were present. The black solid was filtered off, dried in vacuo (66.2% yield), and shown by determination of Pd to be PdI_2.

(B) Treatment of PdI_2 with CO. When suspension of PdI_2 (0.505 g, 1.40 mmol) in toluene (20 cm^3) was kept at 24.0 ° C under one atmosphere pressure carbon monoxide there was a small take up (0.11 mmol) of the gas, presumably owing to chemisorption. No carbonyl stretching vibrations were observed either in the solid or in solution. Similar attempts were made at high pressure at 50 ° C (for example, 0.341 g of PdI_2 in toluene (15 cm^3) for 20 h with carbon monoxide pressurized at 90 atm) were also unsuccessful. The mixture was subsequently cooled and filtered (by the same procedure described for $Pd_2Br_4(CO)_2$ and the black solid recovered found to be uncharged PdI_2. No carbonyl bands were observed in the solution.

(C) Preparation of $[PdI_3(CO)]^-$. Rapid formation of the carbonyl anion was observed from PdI_2 and CO at atmospheric pressure in the presence of a stoicheiometric amount of I^-. Under an atmosphere pressure of carbon monoxide, 0.503 g (1.40 mmol) of PdI_2 was introduced in a gas-volumetric apparatus together with *sym*-$C_2H_2Cl_4$ (20 cm^3) and 0.523 g (1.41 mmol) of $[N\text{-}n\text{-}Bu_4]I$. Rapid absorption of CO occurred at 24.0 ° C, corresponding to about 80% of the amount expected for formation of $[PdI_3(CO)]^-$. Addition of a second equivalent of NBu_4I caused no significant evolution of carbon monoxide. The IR spectrum of the solution showed the presence of an intense carbonyl band at 2015 cm^{-1}.

For preparative purposes the following procedure was used. Palladium(II) iodide (0.535 g, 1.49 mmol) was suspended in 20 cm^3 of *sym*-$C_2H_2Cl_4$. Upon addition of 0.535 g (1.45 mmol) of NBu_4I, the suspended PdI_2 dissolved to give a deep red solution. Carbon monoxide was introduced at atmospheric pressure into the flask and the solution was stirred at room temperature for 3 h. The IR spectrum showed the $\nu(CO)$ band from the $[PdI_3(CO)]^-$ anion. Upon addition of n-heptane, the tetrabutylammonium derivative separated, and was filtered off then dried in vacuo in a stream of CO (61.3% yield).

The red-violet solid is sparingly soluble in hydrocarbons. It loses CO in solution and in the solid state. Solutions in sym-$C_2H_2Cl_4$ kept under reduced pressure showed a decrease in the 2105 cm^{-1} band. A sample of the solid (0.660 g) was introduced together with 20 cm^3 of sym-$C_2H_2Cl_4$ presaturated with CO into a sealed thin-walled flask attacked to a gas-volumetric apparatus, at 24.0 °C, 0.37 mmol of CO were found to be absorbed. Treatment with PPh_3 caused evolution of 0.77 mmol of CO, corresponding to a CO content of 3.3% (calcd. for $NBu_4[PdI_3(CO)]$, $C_{17}H_{36}I_3NOPd$: CO, 3.7%).

Preparation, X-ray data collection and reduction for $[N\text{-}n\text{-}Bu_4][PdCl_3(CO)]$ and for $[N\text{-}n\text{-}Bu_4][PdBr_3(CO)] \cdot C_2H_2Cl_4$

These compounds were prepared by a slight modification of the published procedure [4], as described above for $NBu_4[PdI_3(CO)]$. Thus $PdCl_2$ (1.199 g, 6.76 mmol) was suspended in sym-$C_2H_2Cl_4$ under nitrogen and treated with 14.5 cm^3 of a 0.48 *M* solution of $[N\text{-n-}Bu_4]Cl$ in the same solvent. Upon heating, a deep red solution was formed, and this was treated with CO at atmospheric pressure. After 2 h, the IR spectrum showed the intense carbonyl band at 2135 cm^{-1} (see Table 1) due to $[PdCl_3(CO)]^-$. The deep red solution was filtered and 30 cm of n-heptane were added. The red precipitate was filtered off and dried in vacuo (1.38 g, 42.2% yield).

The bromo derivative was prepared similarly in 63% yield. Crystals of both compounds for the X-ray studies were obtained by keeping the mother liquors from the preparations at about 5 °C. The crystals are air sensitive, and so were sealed in thin-walled glass capillaries which were mounted on a Philips PW 1100 four-circle diffractometer equipped with graphite-monochromatized Mo-K_α radiation. The results from automatic peak search, centering and indexing procedures were consistent with a monoclinic lattice in the case of $[N\text{-n-}Bu_4][PdCl_3(CO)]$ and with a triclinic lattice in the case of $NBu_4[PdBr_3(CO)] \cdot C_2H_2Cl_4$. For the former compound, the systematic extinctions observed, $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, identified the space group as $P2_1/n$, a non-standard setting of C^5_{2h}, No. 14. For $NBu_4[PdBr_3(CO)] \cdot C_2H_2Cl_4$, the absence of systematic extinctions and a $\bar{1}$ diffraction symmetry were consistent with the space group $P1$ and $P\bar{1}$. The statistical tests for the normalized structure factors E clearly pointed to the centrosymmetric space

Table 1

IR carbonyl stretching vibrations for palladium(II) carbonyl complexes

Compound	$\tilde{\nu}$(CO) (cm^{-1})			
	Toluene	CH_2Cl_2	sym-$C_2H_2Cl_4$	Reference
$Pd_2Cl_4(CO)_2$	2160	2166		This work, 6
$Pd_2Br_4(CO)_2$	2148			This work
$[PdCl_3(CO)]^-$ [a]		2132	2135	4,6
$[PdBr_3(CO)]^-$ [a]		2120	2125	This work, 4
$[PdI_3(CO)]^-$ [a]			2105	This work

[a] Tetra-n-butylammonium derivative.

group $P\bar{1}$, which was therefore assumed and subsequently confirmed by the successful structure determination. The unit-cell dimensions, which were obtained by a least-squares refinement of the setting angles of 25 reflections, are listed in Table 2, together with a summary of the crystal data and details of data collection and structure analysis. The intensity of a control reflection was measured periodically to assess possible crystal decomposition or movement but showed only random statistical fluctuations for both compounds. In each case, the intensities were converted into relative structure amplitudes by routine procedures, including the application of an empirical absorption correction based on ψ scans of reflections with the diffractometer angle χ near 90°.

The structures were solved by the heavy-atom method procedure, with the positions of the palladium atom found from Patterson syntheses. Alternating difference Fourier maps and structure factor calculations revealed the remaining

Table 2

Experimental details of the X-ray diffractometric study

Compound	$[\text{N-n-Bu}_4][\text{PdCl}_3(\text{CO})]$	$[\text{N-n-Bu}_4][\text{PdBr}_3(\text{CO})]\cdot\text{C}_2\text{H}_2\text{Cl}_4$
Formula	$C_{17}H_{36}Cl_3NOPd$	$C_{19}H_{38}Br_3Cl_4NOPd$
FW	483.24	784.44
space group	$P2_1/n$	$P\bar{1}$
a, Å	18.231(10)	16.667(10)
b, Å	8.889(4)	10.376(8)
c, Å	14.978(8)	9.644(7)
α, deg	90	74.27(3)
β, deg	104.88(2)	75.12(3)
γ, deg	90	83.27(4)
V, Å^3	2346(2)	1549(2)
Z	4	2
d_{calcd}, g cm^{-3}	1.368	1.681
$\mu(\text{Mo-}K_\alpha)$, cm^{-1}	11.29	47.84
Crystal size, mm	0.11 × 0.38 × 1.20	0.33 × 0.66 × 1.05
Collection region	$\pm h, +k, +l$	$\pm h, \pm k, +l$
θ range, deg	3.0–26.0	2.0–30.0
Scan speed, deg·s^{-1}	0.100	0.070
Scan width, deg	1.20	1.40
Standard reflection	2 0 6	$5\ \bar{1}\ 2$
frequency	every 60 min	every 90 min
No. of reflections measured	5092 [a]	8955
No. of unique reflections	4610	8934
No. of observed reflections	2035	2286
Highest and lowest peaks of final ΔF map, e Å^{-3}	0.40 −0.39	1.83 −1.25
No. of parameters refined	328	232
Data to parameter ratio	6.20/1	9.85/1
R [b]	0.0397	0.0886
R_w [c]	0.0498	0.1255
GOF	0.9741	1.5356

[a] Including 314 systematically absent reflections. [b] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [c] $R_w = [\Sigma w|\Delta F|^2/\Sigma w F_o^2]^{1/2}$. Features common to both determinations: Mo-K_α radiation (λ 0.71069 Å); scan type: ω-2θ, criterion for data omission: $I < 3\sigma(I)$.

Table 3

Fractional atomic coordinates ($\times 10^5$ for Pd, $\times 10^4$ for Cl, N, O and C) for $[\text{N-n-Bu}_4][\text{PdCl}_3(\text{CO})]$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
Pd	28253(3)	12742(7)	74(4)	C(7)	326(7)	−561(11)	1636(6)
Cl(1)	3692(1)	1143(2)	1409(1)	C(8)	112(8)	−2176(11)	1375(7)
Cl(2)	3525(1)	3020(3)	−546(2)	C(9)	51(6)	−2511(10)	367(6)
Cl(3)	2038(2)	−414(3)	450(2)	C(10)	517(4)	1237(10)	4020(5)
O	1731(5)	1341(12)	−1854(6)	C(11)	806(6)	2600(10)	4601(6)
N	617(3)	1236(6)	3038(3)	C(12)	695(5)	2393(11)	5562(6)
C(1)	2135(6)	1337(13)	−1155(8)	C(13)	945(6)	3709(11)	6196(6)
C(2)	168(4)	2511(10)	2473(6)	C(14)	1438(4)	1476(10)	3026(6)
C(3)	−677(6)	2476(11)	2329(7)	C(15)	2002(5)	344(12)	3581(8)
C(4)	−1065(5)	3748(13)	1691(7)	C(16)	2771(6)	607(14)	3413(9)
C(5)	−1911(6)	3772(14)	1555(9)	C(17)	3354(7)	−506(16)	3918(10)
C(6)	336(4)	−290(8)	2632(5)				

non-hydrogen atoms. The bromo compound was found to have a lattice tetrachloroethane molecule which was somewhat disordered and probably had partial occupancy. Refinement was by full-matrix least-squares calculations based upon *F*. The function minimized was $\Sigma w|\Delta F^2|$. For $\text{NBu}_4[\text{PdCl}_3(\text{CO})]$, anisotropic thermal parameters were used for all non-hydrogen atoms and isotropic ones for hydrogens, which were located in a difference Fourier map or placed in calculated positions. For $\text{NBu}_4[\text{PdBr}_3(\text{CO})] \cdot \text{C}_2\text{H}_2\text{Cl}_4$, all the anionic and cationic non-hydrogen atoms were allowed to vibrate anisotropically, while the atoms of the tetrachloroethane molecule were refined isotropically. No hydrogen atoms were included in the refinement of the bromo derivative. The values of the discrepancy indices at convergence are listed in Table 2. A final difference Fourier map revealed significant in either structure except for some peaks near the solvent in the bromo complex. The values of the atomic scattering factors used in the calculations are

Table 4

Fractional atomic coordinates ($\times 10^4$) for $[\text{N-n-Bu}_4][\text{PdBr}_3(\text{CO})] \cdot \text{C}_2\text{H}_2\text{Cl}_4$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
Pd	1793(1)	2141(2)	3296(2)	C(10)	2139(15)	6260(20)	5339(22)
Br(1)	2488(2)	4223(3)	2294(3)	C(11)	3000(19)	6943(26)	4774(27)
Br(2)	2693(2)	1232(3)	4981(3)	C(12)	3026(25)	7688(39)	3052(39)
Br(3)	788(2)	2805(3)	1763(3)	C(13)	3841(31)	8309(52)	2454(46)
O	954(12)	−433(20)	4636(26)	C(14)	1175(13)	4901(18)	7562(21)
N	2047(10)	5382(15)	6971(19)	C(15)	992(13)	4003(22)	6665(27)
C(1)	1252(15)	525(26)	4085(29)	C(16)	98(17)	3537(28)	7466(33)
C(2)	2193(13)	6173(19)	8009(23)	C(17)	−185(19)	2577(32)	6651(40)
C(3)	1634(13)	7452(20)	8036(26)	Cl(1)	5735(6)	1301(9)	3560(10)
C(4)	1822(16)	8107(22)	9163(29)	Cl(2)	4745(9)	1597(13)	1280(15)
C(5)	1252(17)	9422(24)	9228(31)	Cl(3)	4825(8)	4174(12)	3843(13)
C(6)	2726(12)	4268(22)	6879(26)	Cl(4)	5797(7)	3976(10)	866(11)
C(7)	2613(14)	3113(22)	8384(27)	C(18)	4828(23)	2147(36)	3125(41)
C(8)	3416(20)	2170(30)	8216(36)	C(19)	4799(27)	3457(40)	2010(46)
C(9)	3290(26)	990(39)	9476(51)				

taken from the usual tabulation [7] and the effects of the anomalous dispersion were included for all non-hydrogen atoms. Computing was performed on the Cray X-MP/12 of CINECA (Casalecchio, Bologna). The SHELX 76 package [8] was used for solution and refinement, PARST [9] for molecular geometry calculations, and ORTEP [10] for drawings. Final atom coordinates are shown in Tables 3 and 4, and important bond lengths and angles in Tables 4 and 6. Tables of H-atom coordinates (for $NBu_4[PdCl_3(CO)]$), thermal parameters, observed and calculated structure factors, and a complete list of bond lengths and angles are available from the authors.

Results and discussion

Comparison between platinum(II) and palladium(II) complexes is an interesting subject in itself. Furthermore, information was expected from this study about the variation in stability with the identity of the halide. Because of the generally lower stability of palladium carbonyl complexes compared with their platinum analogues, the effects of the halide were expected to be larger for palladium.

Several years after the first isolation [6] of $Pd_2Cl_4(CO)_2$ we have succeeded now in preparing $Pd_2Br_4(CO)_2$, although it was always contaminated by $PdBr_2$ formed by loss of coordinated carbon monoxide. Equilibrium 1 is considerably shifted to the left for X = Br compared with that for the corresponding chloride. $Pd_2Br_4(CO)_2$ was obtained from $PdBr_2$ and CO under pressure and quenching the solution at

$$2\ PdX_{2(s)} + 2\ CO \rightleftharpoons Pd_2X_4(CO)_2 \tag{1}$$

dry-ice temperature. The bromo complex was finally isolated at low temperature. Since only one CO stretching vibration (see Table 1) was observed for $Pd_2Br_4(CO)_2$, and this was at a lower frequency than that from $Pd_2Cl_4(CO)$, there is little doubt that the bromo derivative has the same structure with idealized C_{2h} symmetry as was found [1] for $Pt_2I_4(CO)_2$. No carbonyl palladium species were observed upon attempted carbonylation of PdI_2 at elevated pressures of CO.

These observations can be rationalized in terms of a decreasing tendency of the palladium halides to form Pd–CO bonds along the sequence Cl > Br > I. In other words, if equilibrium 1 operates for the three halocarbonyl complexes, $Pd_2I_4(CO)_2$ can be expected to be detectable only at very high pressure of CO.

Further confirmation of these conclusions came from the experiments with the anionic $[PdX_3(CO)]^-$ species. The chloro and bromo derivatives had been prepared earlier [4], but the iodo complex is new. The formation of $[PdI_3(CO)]^-$ can be visualized to involve equilibria 2 and 3, X = I. The iodo carbonyl complex was found to be much less stable than the corresponding bromo and chloro species, loss of CO being observed both in solution and in the solid state. Gas-volumetric

$$2\ PdX_2 + 2\ X^- \rightleftharpoons Pd_2X_6^{2-} \tag{2}$$

$$Pd_2X_6^{2-} + 2\ CO \rightleftharpoons 2\ [PdX_3(CO)]^- \tag{3}$$

measurements on the PdI_2/CO system showed that the amount of CO adsorbed is not greatly affected by the concentration of I^- in the concentration range 0.07–0.1 *M* up to a 4/1 molar ratio of I to Pd, implying that no significant concentration of PdI_4^{2-} is present in equilibrium with $Pd_2I_6^{2-}$ under these conditions.

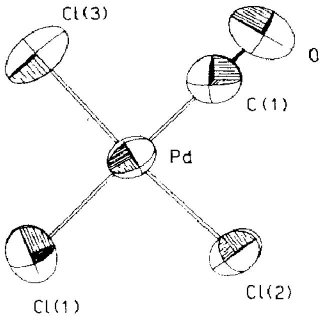

Fig. 1. Perspective view of the $[PdCl_3(CO)]^-$ anion in $[N\text{-}n\text{-}Bu_4][PdCl_3(CO)]$ with atoms drawn with 50% probability thermal ellipsoids.

The crystal and molecular structures of both $[N\text{-}n\text{-}Bu_4][PdCl_3(CO)]$ and $[N\text{-}n\text{-}Bu_4][PdBr_3(CO)]$ have been determined. The crystals of both compounds consist of discrete $[PdX_3(CO)]^-$ anions and NBu_4^+ cations. ORTEP drawings and atom numbering schemes for the anions are shown in Fig. 1 and 2. The coordination geometry about the palladium atom in both anions is essentially square planar, and involves three halogens and one carbonyl group. The maximum deviation from exact planarity is 0.09 Å for $[PdCl_3(CO)]^-$ and 0.02 Å for $[PdBr_3(CO)]^-$, and in both cases is at the carbon atom. The metal atom is displaced by only 0.02 Å from the best plane through the four coordinated atoms. The angles at palladium, all close to the expected square planar values of 90 and 180 ° C, deserve some comment. As indicated by the data quoted in Tables 5 and 6, for each compound there is a small but significant difference between the *cis*-angles and also between *trans* angles. In the case of the *cis* angles, the X–Pd–X ones are slightly obtuse, unlike the X–Pd–C angles which are slightly acute. In the case of the *trans* angles, the X–Pd–X angle is slightly more bent than the X–Pd–X angle. These features, can be readily accounted for in terms of steric interactions, and in keeping with this the differences increase on going from the chloride to the bromide.

The Pd–Cl and Pd–Br bond lengths the two structures (mean bond lengths: 2.289 Å for $[PdCl_3(CO)]^-$ and 2.423 Å for the bromo analogue) are close to the range of values observed for other chloro and bromo derivatives of palladium(II). Thus a weighted mean Pd–Cl distance of 2.300(2) Å has been derived from data for

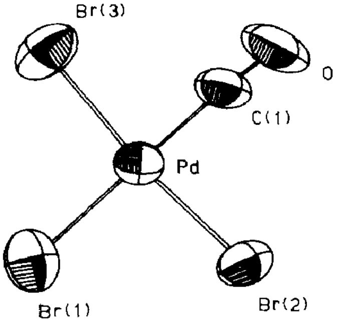

Fig. 2. Perspective view of the $[PdBr_3(CO)]^-$ anion in $[N\text{-}n\text{-}Bu_4][PdBr_3(CO)]\cdot C_2H_2Cl_4$ with atoms drawn with 50% probability thermal ellipsoids.

Table 5

Selected bond distances (Å) and angles (deg) for [N-n-Bu$_4$][PdCl$_3$(CO)]

Pd–Cl(1)	2.284(2)	N–C(2)	1.52(1)
Pd–Cl(2)	2.295(3)	N–C(6)	1.52(1)
Pd–Cl(3)	2.289(3)	N–C(10)	1.53(1)
Pd–C(1)	1.87(1)	N–C(14)	1.52(1)
C(1)–O	1.11(1)		
Cl(1)–Pd–Cl(2)	92.8(1)	C(2)–N–C(6)	111.4(5)
Cl(1)–Pd–Cl(3)	92.1(1)	C(2)–N–C(10)	110.8(6)
Cl(1)–Pd–C(1)	178.1(4)	C(2)–N–C(14)	106.3(5)
Cl(2)–Pd–Cl(3)	174.9(1)	C(6)–N–C(10)	105.9(5)
Cl(2)–Pd–C(1)	87.0(4)	C(6)–N–C(14)	110.7(5)
Cl(3)–Pd–C(1)	88.1(4)	C(10)–N–C(14)	111.9(5)
Pd–C(1)–O	178(1)		

thirteen palladium(II) complexes having *trans* chloride ligands [11]. Other relevant Pd–X distances are the Pd–Cl distances of 2.287(2) and 2.294(2) Å in diguanidinium tetrachloropalladite(II) [12], and the Pd–Br distances of 2.431(1) and 2.412(1) Å in *trans*-dibromobis[2,-(2′-thienyl)pyridine]palladium(II) [13] and dibromobis(iminodiacetamido)palladium(II) [14], respectively. These values are close to the sums of the corresponding Van der Waals radii. However, it is noteworthy that in both of our compounds the Pd–X bond opposite the carbonyl group is approximately 0.01 Å shorter than those involving the two mutually *trans* halides, contrary to what would be expected on the basis of the high *trans* effect of CO [15], but one data is not sufficiently accurate to place much significance to these differences.

Our data can be compared with those [16] for the analoguous compound of platinum(II), NBu$_4$[PtCl$_3$(CO)]. In this case also, the Pt–Cl distance (2.289(3) Å) *trans* to the CO ligand is substantially identical, within experimental error, to those for the other two mutually *trans* chlorides. Also noteworthy is that the Pd–CO bond distances are substantially unaffected by the change of the halide, and comparison of our solid state data with those for the platinum(II) complex shows that the

Table 6

Selected bond distances (Å) and angles (deg) for [N-n-Bu$_4$][PdBr$_3$(CO)]·C$_2$H$_2$Cl$_4$

Pd–Br(1)	2.413(4)	N–C(2)	1.53(3)
Pd–Br(2)	2.423(4)	N–C(6)	1.52(2)
Pd–Br(3)	2.432(4)	N–C(10)	1.57(2)
Pd–C(1)	1.87(3)	N–C(14)	1.51(3)
C(1)–O	1.10(3)		
Br(1)–Pd–Br(2)	93.0(2)	C(2)–N–C(6)	108(2)
Br(1)–Pd–Br(3)	94.1(2)	C(2)–N–C(10)	112(2)
Br(1)–Pd–C(1)	179.7(8)	C(2)–N–C(14)	107(2)
Br(2)–Pd–Br(3)	172.8(2)	C(6)–N–C(10)	105(2)
Br(2)–Pd–C(1)	86.8(8)	C(6)–N–C(14)	114(2)
Br(3)–Pd–C(1)	86.0(8)	C(10)–N–C(14)	109(2)
Pd–C(1)–O	175(2)		

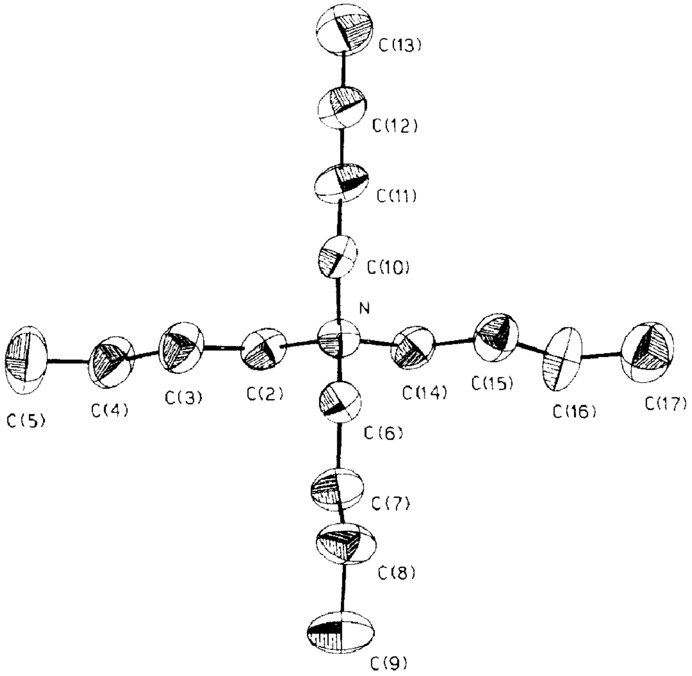

Fig. 3. Perspective view of the $[N\text{-n-}Bu_4]^+$ cation in $[N\text{-n-}Bu_4][PdCl_3(CO)]$. Thermal ellipsoids are shown at the 50% probability level.

M–CO distance for palladium (1.87(1) Å, X = Cl; 1.87(3) Å, X = Br) is similar to that reported [16] for the platinum(II) system (Pt–CO, 1.82(1) Å).

The asymmetric unit of $[N\text{-n-}Bu_4][PdBr_3(CO)]$ contains a tetrachloroethane lattice molecule, which was found to be, as usual, somewhat disordered, as evidenced by some unusual bond lengths as well as by the high thermal motion.

It is interesting to note that the $[N\text{-n-}Bu_4]^+$ cation adopts a different conformation in the two compounds. The overall idealized symmetry of the cation is D_{2d} in $[N\text{-n-}Bu_4][PdCl_3(CO)]$ and S_4 in $[N\text{-n-}Bu_4][PdBr_3(CO)]$, as shown in Fig. 3 and 4,

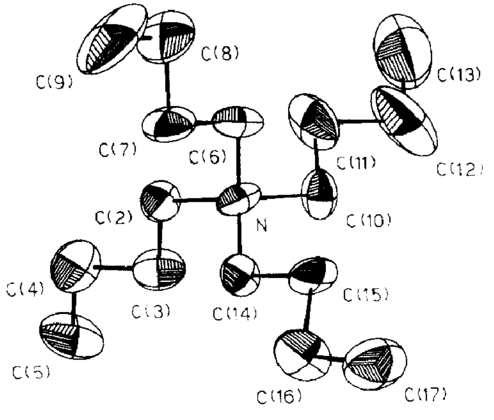

Fig. 4. Perspective view of the $[N\text{-n-}Bu_4]^+$ cation in $[N\text{-n-}Bu_4][PdBr_3(CO)]\cdot C_2H_2Cl_4$. Thermal ellipsoids are shown at the 40% probability level.

respectively. This is probably due to packing requirements, and possibly also related to the fact that the bromo derivative contains lattice solvent molecules. In both compounds the structural parameters for the cation are mostly in the range of expected values or very similar to those in other tetra-n-butylammonium derivatives [17].

The molecular packing for both compounds is mainly determined by Van der Waals interactions.

Conclusions

We summarize here the conclusions that can be drawn from the results in this paper and those in the preceding one. Our findings appear to confirm the earlier suggestion by Malatesta and Naldini [18] that the stability of halocarbonyl complexes of platinum(II) decreases in the sequence Cl > Br > I. The results for palladium confirm that the trend of stability is similar for both metals. The information presented for the iodo derivatives have revealed that the values of $\tilde{\nu}(CO)$ and $J(Pt-C)$ decrease in the same sequence as the halide ligands are varied. Furthermore, the σ-component of the Pt–CO bond, as indicated by the $J(Pt-C)$ parameter, is affected by the nature of the halide ligand and decreases in the same sequence.

We have shown that as a ligand CO competes successfully with the halide for coordination position around platinum(II). The halide-bridged structure of PtX_2 (M = Pt in equation 4) can be converted into $Pt_2X_4(CO)_2$ species or the monomeric species $PtX_2(CO)_2$. The latter are thermodynamically stable with respect to $Pt_2X_4(CO)_2$ and CO, i.e. equilibrium 5, M = Pt, is completely shifted to the right,

$$2\ MX_{2(s)} + 2\ CO \rightleftharpoons M_2X_4(CO)_2 \tag{4}$$

$$M_2X_4(CO)_2 + 2\ CO \rightleftharpoons 2\ MX_2(CO)_2 \tag{5}$$

independent of the nature of X, and the corresponding equilibrium constants are immeasurably large in spite of the presumably unfavourable entropy change. Conversion of the centrosymmetric halide-bridged dimeric $Pt_2X_4(CO)_2$ into $PtX_2(CO)_2$ involves the loss of two Pt–X bonds per platinum for the dimer and to formation of one Pt–X and one Pt–CO bond for the monomer; the net difference in bond energies between products reagents involving the formation and rupture is given by $(Pt-X_t + Pt-CO_t) - 2\ (Pt-X_b)$.

The stabilities of the dimeric carbonyl complexes $Pd_2X_4(CO)_2$ relative to PdX_2 and CO (see equation 4, M = Pd) decreases along the series Cl > Br > I. Thus, the values of $\tilde{\nu}(CO)$ and $J(Pt-C)$ for the platinum complexes on the one hand and the chemical behaviour observed for palladium on the other are consistent. Palladium and platinum should, because of their similar electron counts, give isostructural complexes for a given oxidation state. On the other hand, bond energies are expected to increase from palladium to platinum, as is usual for transition elements on going from 4*d* to 5*d* systems. Thus, the failure to observe the monomeric $PdX_2(CO)_2$ and the iodo derivative $Pd_2I_4(CO)_2$ can be attributed to an intrinsically weaker Pd–CO bond: it is possible that these compounds would become observable at very high CO pressures through equilibria 4 and 5, M = Pd.

The new results are consistent with our earlier proposal [19] that the σ-component predominates in both the Pd–CO and the Pt–CO bonds. It is of interest that ethylene was recently suggested [20] to be a strong σ-donor and a weak π-acceptor towards platinum(II) in $[PtCl_3(C_2H_4)]^-$. The exceptionally high reactivity of platinum and palladium carbonyl complexes towards nucleophiles such as water and amines may also be a consequence of the fact that the dominant σ-component induces an unusually high polarization in the M–CO bond.

A recent theoretical calculation [21] on tetracarbonyl species $M(CO)_4$, ($M = Ni$, Pd, Pt) has indicated that the "intrinsic mean bond energy" decreases in the sequence $Ni > Pd > Pt$, and that the σ-interactions are somewhat stronger for $M = Ni$ than for $M = Pd$ and Pt.

Our data for palladium(II) and platinum(II) species are consistent with a considerably higher energy for the Pt–CO than for the Pd–CO bond. Increase in the oxidation state of the metal will further disfavour the σ-contribution to the bond. Our general conclusions therefore are consistent with both the experimental results and the theoretical calculations on these and related systems.

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