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that they prefer to interact with the tungsten $6p_z$ orbital (e.g. halides), and whose σ interaction with tungsten is not reinforced by an accompanying π interaction (e.g. hydride, methyl, amines, acetate).

Acknowledgment. The authors are indebted to Prof. M. A. Bennett for stimulating discussions during his visit to the Universität Würzburg. Thanks are due to Dr. D. Scheutzow for recording the 100-MHz ^{13}C NMR spectra. This work was supported by the Fonds der Chemischen Industrie.

Registry No. $W(CO)_5H^-$, 77227-36-2; $W(CO)_5CH_3^-$, 57574-50-2; $W(CO)_5CPh_2$, 50276-12-5; $W(CO)_6$, 14040-11-0; $W(CO)_5CN^-$, 14971-29-0; $W(CO)_5(dmf)$, 76096-25-8; $W(CO)_5C_6H_{11}NH_2$, 61779-22-4; $W(CO)_5C_5H_5N$, 14586-49-3; $W(CO)_5CH_3CN$, 15096-68-1; $W(CO)_5NCS^-$, 45113-96-0; $W(CO)_5PMe_3$, 26555-11-3; $W(CO)_5P(NMe_2)_3$, 19976-82-0; $W(CO)_5P(OMe)_3$, 23306-42-5; $W(CO)_5PPh_3$, 15444-65-2; $W(CO)_5P(OPh)_3$, 23306-41-4; $W(CO)_5AsPh_3$, 29743-02-0; $W(CO)_5SbPh_3$, 29743-03-1; $W(CO)_5OC(O)CH_3^-$, 45146-15-4; $W(CO)_5SH^-$, 65198-80-3; $W(CO)_5SC(S)H^-$, 77227-31-7; $W(CO)_5Cl^-$, 14911-74-1; $W(CO)_5Br^-$, 15131-04-1; $W(CO)_5I^-$, 14911-58-1.

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Formation of Palladium(II) and Palladium(I) Carbonyl Halo Complexes

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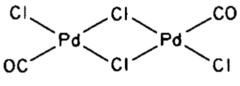
The preparation of the dimeric palladium(II) chloro carbonyl $Pd_2(CO)_2Cl_4$ from $PdCl_2$ and carbon monoxide in thionyl chloride as solvent was studied as a function of temperature and carbon monoxide partial pressure. The reaction, $2PdCl_{2(s)} + 2CO_{(SOCl_2)} \rightleftarrows Pd_2(CO)_2Cl_{4(SOCl_2)}$, was found to be exothermic with $\Delta H° = -13.6 \pm 0.2$ kcal/mol of dimer and with $\Delta S° = -30.8 \pm 0.8$ eu. The enthalpy change, together with the accepted mean Pd–Cl bond energies and other peripheral information, has been used to deduce a value of about 24 kcal for the Pd–CO bond energy in the palladium(II) carbonyl derivative. This is compared with the metal–CO bond energies of other metal carbonyl derivatives. A high-yield synthesis of the polymeric palladium(I) chloro carbonyl $[Pd(CO)Cl]_n$ is also reported, consisting of treating $PdCl_2$ or $Pd_2(CO)_2Cl_4$ with CO in acetic anhydride as solvent.

In an earlier publication[1] we had established the existence of the elusive[2-5] dimeric chloro carbonyl complex $Pd_2(CO)_2Cl_4$ assumed to have the trans structure **1**. Its extremely high ν_{CO} value (2163 cm^{-1} in thionyl chloride) suggested a strongly reduced π-back-bonding contribution and a palladium–CO bond presumably weaker and/or more reactive than usually assumed for other metals of lower d^n configurations, i.e. toward the middle part of the transition series. Palladium thus appears to have unique behavior as far as its bonding to CO is concerned, a feature possibly typical of silver(I), for which no stable isolable carbonyl complexes are known.[6]



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A study of the formation of $Pd_2(CO)_2Cl_4$ from $PdCl_2$ and carbon monoxide and the measurement of some thermodynamic parameters, which are the subjects of this paper, was therefore in order. In addition a high-yield preparation of $[Pd(CO)Cl]_n$ is reported.

Experimental Section

The chloro carbonyl derivative $Pd_2(CO)_2Cl_4$ was prepared as previously described.[1] Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified carbon monoxide or nitrogen. Solvents were dried prior to use by the conventional methods. The IR spectra were measured with a Perkin-Elmer Model 283 instrument equipped with a grating monochromator, and each spectrum was calibrated with both CO and water vapor: the wavenumber values are believed to be accurate to ±1 cm^{-1}. The experiments were carried out in stainless-steel nickel–chrome (18/8) autoclaves, which were found to be unaffected by thionyl chloride up to 120 °C. Caution must be taken, however, to avoid contact of the autoclave with moisture prior to complete evaporation of the solvent in vacuo after each experiment.

Table I. Solubilities of Carbon Monoxide and $Pd_2(CO)_2Cl_4$ in Thionyl Chloride

CO				$Pd_2(CO)_2Cl_4$		
t, °C	p_{CO},[a] atm	$10^3[CO]$,[b] M	$-\ln X_2$[c]	t, °C	$[Pd_2(CO)_2Cl_4]$, M	$-\ln K$[d]
10.1	4.1	8.22	7.43	−10.00	0.139	1.97
23.2	0.85	6.30	7.68	0.0	0.195	1.64
31.5	0.75	6.27	7.67	14.0	0.349	1.05
42.5	5.1	6.73	7.60	16.5	0.363	1.01
51.7	5.0	7.33	7.50			
58.8	5.0	6.24	7.65			

[a] For experiments at superatmospheric pressure, this is the manometer reading plus 1 atm, corrected for the vapor pressure of the solvent. [b] This is the solubility normalized to 1 atm of pressure. [c] X_2 is the mole fraction of CO dissolved; see ref 8. [d] This is referring to the equilibrium $Pd_2(CO)_2Cl_{4(s)} \rightleftarrows Pd_2(CO)_2Cl_{4(SOCl_2)}$. From the $-\ln K$ vs. $1/T$ plot, the extrapolated concentrations of $Pd_2(CO)_2Cl_4$ were found to be 0.49 and 0.57 M, at 25 and 30 °C, respectively. From the slope of the same plot, an enthalpy change for the solubilization of $Pd_2(CO)_2Cl_4$ of +5.8 ± 0.2 kcal/mol was calculated.

Solubility of Carbon Monoxide in Thionyl Chloride. The solubility data are in Table I. For experiments at superatmospheric pressure, the autoclave (120.9-cm^3 capacity) was charged by suction with a known volume of thionyl chloride, which was then degassed by connecting the autoclave to a vacuum system and evaporating a small known amount of the liquid into a cold trap. The final volume of thionyl chloride in the autoclave was then determined exactly (the experiments were carried out with volumes of solvent between 85 and 95 cm^3). The autoclave was then introduced into an oil bath maintained at a constant temperature identical with that of a carbon monoxide pressure tank connected to the autoclave with a short stainless-steel high-pressure capillary tube. While the autoclave was maintained in a fixed position with the smallest possible surface area for the internal liquid, carbon monoxide from the tank was rapidly

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Table II. Equilibrium Data for Reaction 1

run no.	t, °C	T, K	$10^3/T$, K^{-1}	p_{CO},[a] atm	$10^3 \times$ $[Pd_2(CO)_2Cl_4]$, M	$10^3 \times$ [CO],[b] M	K,[c] M^{-1}	$-\ln K$	$-\Delta G°$, kcal/mol
1	35.0	308.2	3.245	0.749	22.0	4.71	991.0	−6.90	4.23
2	41.5	314.7	3.178	0.752	14.6	4.73	652.0	−6.48	4.05
3	43.0	316.2	3.162	4.68	31.8	29.4	368.0	−5.90	3.71
4	47.3	320.5	3.120	0.691	8.3	4.35	439.0	−6.08	3.87
5	60.0	333.2	3.001	4.08	72.6	25.7	110.0	−4.70	3.11
6	80.0	353.2	2.831	8.82	144.7	55.4	47.1	−3.85	2.70
7	93.0	366.2	2.731	11.73	152.9	73.8	28.1	−3.33	2.42
8	111.0	384.2	2.603	8.09	26.4	50.9	10.2	−2.32	1.77
9	115.2	388.4	2.574	4.62	8.3	29.0	9.9	−2.29	1.76

[a] This is the partial pressure of CO (total pressure corrected for the vapor pressure of the solvent). [b] The solubility of CO (see third column of Table I) was found to be substantially independent of temperature and assumed to be proportional to its partial pressure in the range 0.7–12 atm, taking the solubility measured at 23.2 °C and at p_{CO} = 0.85 atm as reference. [c] The activity coefficients for dissolved species were assumed to be 1.

transferred to the autoclave up to a given pressure. The rocking movement was then started, and both the pressure drop and the equilibrium pressure were noted. From the known free volume, the density, and the vapor pressure[7] of the liquid at the temperature of the experiment, the number of moles of CO dissolved per unit volume of solution was calculated.

The solubility of CO at atmospheric pressure was measured in a thermostated gas-volumetric apparatus: the volume of CO dissolved in a given volume of degassed thionyl chloride was measured as the difference between the volume of CO introduced into the reactor at atmospheric pressure and the free volume. After correction for the density and vapor pressure of the solvent,[7] the molar concentration of CO dissolved was calculated. Also reported in Table I are the −ln X_2 values, X_2 being the mole fraction of CO dissolved, since this function has been frequently used to calculate the heat of solubilization of gases in various solvents.[8]

Apparatus and Procedure for Measurement of the Equilibria. The temperature dependence of equilibrium 1 was studied by monitoring

$$2PdCl_{2(s)} + 2CO_{(SOCl_2)} \rightleftarrows Pd_2(CO)_2Cl_{4(SOCl_2)} \quad (1)$$

the 2163-cm^{-1} carbonyl stretching vibration of the dimer, ϵ = 1415 M^{-1} cm^{-1}, which was found to obey the Lambert–Beer law. The experiments were carried out by the following procedure. A 120.9-cm^3 autoclave was charged with $PdCl_2$ and evacuated to about 5 × 10^{-2} mmHg. Thionyl chloride (40.0 cm^3) was then introduced into the autoclave by suction, and subsequently the autoclave was connected to a vacuum system in order to degas the solvent. The volume of solvent evaporated and condensed into a cold trap was noted, and then carbon monoxide was compressed into the autoclave, whose contents were then stirred by rocking in a thermostated oil bath. After equilibrium had been reached, the autoclave was rapidly cooled to room temperature and a sample withdrawn for IR analysis by spilling a few milliliters of the solution from the gas inlet of the autoclave. The carbon monoxide was then reset to a new value, and the autoclave was ready for another experiment at a different temperature. The amount of $PdCl_2$ used for each set of experiments was high enough to guarantee the presence of solid starting material in equilibrium with the solution. The IR analysis of the reaction mixture showed the presence of an additional band of small intensity at 2040 cm^{-1} due to COS, in addition to the band at 1804 cm^{-1} typical[9] of $COCl_2$, both arising from the reaction of CO with $SOCl_2$. At the end of each cycle of experiments, the solid in the autoclave was analyzed and found to correspond to $PdCl_2$. The equilibrium data are in Table II, and the −ln K vs. $1/T$ plot is presented in Figure 1, in order to show the density and dispersion of the points.

Solubility of $Pd_2(CO)_2Cl_4$ in Thionyl Chloride. The solubilities of the chloro carbonyl complex were determined by measuring the absorbance of the 2163-cm^{-1} band of saturated solutions from −10 to +16.5 °C. The solutions were maintained in a thermostated bath and stirred under CO for about 0.5 h before the IR absorbance was measured. At higher temperatures, extensive decomposition to $PdCl_2$ occurred and the measurements thus became unreliable. The solubility values are in Table I. From the plot of −ln K for the solubility equilibrium (2) vs. $1/T$, a heat of solution of +5.9 ± 0.2 kcal/mol was calculated.

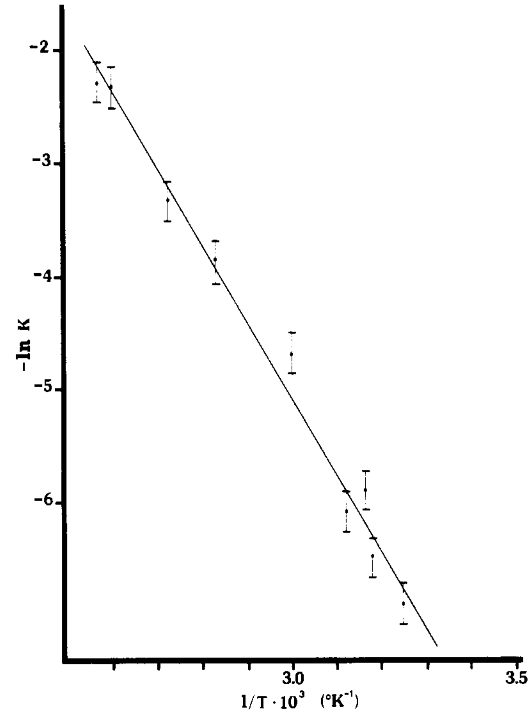

Figure 1. Plot of −ln K vs. $1/T$ for the formation of $Pd_2(CO)_2Cl_4$ from $PdCl_{2(s)}$ and carbon monoxide in thionyl chloride as solvent (eq 1).

$$Pd_2(CO)_2Cl_{4(s)} \rightleftarrows Pd_2(CO)_2Cl_{4(SOCl_2)} \quad (2)$$

Preparation of $[Pd(CO)Cl]_n$. (A) From $Pd_2(CO)_2Cl_4$. The halo carbonyl (0.712 g; 3.47 mmol) was treated with carbon monoxide at atmospheric pressure in acetic anhydride (25 cm^3) as solvent. After the mixture was stirred for 24 h at room temperature, the yellow solid present in suspension was filtered under nitrogen, washed with dichloromethane, and dried in vacuo (0.52 g; 88.3% yield). In a control gas-volumetric experiment, carbon monoxide was found to be absorbed in 4 h in the CO/Pd molar ratio of 0.44.

(B) From $PdCl_2$ and CO. Palladium(II) chloride (2.10 g; 11.84 mmol) was introduced into a stainless-steel magnetically stirred autoclave of 108-cm^3 capacity together with acetic anhydride (25 cm^3) and carbon monoxide at 40 atm. The autoclave was stirred at 18 °C for 40 h, and after the gases were vented, the chloro carbonyl was collected by filtration under nitrogen, washed with dichloromethane, and dried in vacuo (90.9% yield). In control experiments carried out at atmospheric pressure, 1.3 mol of CO/mol of $PdCl_2$ was found to be absorbed at room temperature in 10 days. The compound is sparingly soluble in acetic anhydride and in halogenated solvents and practically insoluble in aliphatic and aromatic hydrocarbons, with

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properties generally corresponding to those already reported for the same compound obtained by different routes,[3] including the carbonyl stretching vibration at 1975 cm^{-1} usually accompanied by another band of low intensity at 2170 cm^{-1}. By treatment with an equimolar amount of NH_2Et_2Cl in *sym*-tetrachloroethane, the compound $[NH_2Et_2]_2[Pd_2(CO)_2Cl_4]$ was obtained. Anal. Calcd for $C_{10}H_{24}Cl_4N_2O_2Pd_2$: C, 21.4; H, 4.3; Cl, 25.4. Found: C, 20.1; H, 4.2; Cl, 26.3. In a gas-volumetric control experiment in the same solvent, the formation of the diethylammonium derivative was found to occur without CO evolution. The compound is characterized by a carbonyl stretching vibration at 1916 cm^{-1} in *sym*-$C_2H_2Cl_4$, and an additional band of small intensity is usually also present at 1980 cm^{-1}.

Results and Discussion

The formation of $Pd_2(CO)_2Cl_4$ from palladium(II) chloride and CO, according to eq 1, was studied in detail, and this allowed the optimum conditions for its preparation to be found. From the temperature dependence of the equilibrium, the reaction was found to be exothermic ($\Delta H° = 13.6 \pm 0.2$ kcal/mol; $\Delta S° = -30.8 \pm 0.8$ eu). The least-squares linear plot (see Figure 1 and Table II) obeyed the expression (3).

$$-\ln K = -6834/T + 15.4 \qquad (3)$$

Taking into consideration that the equilibrium (see eq 4) is favored by higher partial CO pressures and that the extrapolated concentration of a saturated solution of the carbonyl dimer in $SOCl_2$ is about 0.5 M at 25 °C, the thermodynamic parameters show that, at 50 °C (a reasonable reaction rate was observed at this temperature), the equilibrium condition for a solution of that concentration is satisfied by a partial pressure of CO between 5 and 6 atm. Presumably, the partial pressure of CO has a positive effect on the kinetics of the carbonylation reaction (we have confirmed the earlier result[1] that, at room temperature, the carbonylation of $PdCl_2$ is too slow if the partial pressure of CO is 1 atm) so that higher p_{CO}'s are desirable in order to decrease the conversion time.

The thermodynamic parameters for the formation of $Pd_2(CO)_2Cl_4$ according to eq 1 can be related to the steps

$$2PdCl_{2(s)} \rightarrow 2PdCl_{2(g)} \qquad (1a)$$

$$2CO_{(SOCl_2)} \rightleftarrows 2CO_{(g)} \qquad (1b)$$

$$2PdCl_{2(g)} + 2CO_{(g)} \rightarrow 2Pd(CO)Cl_{2(g)} \qquad (1c)$$

$$2Pd(CO)Cl_{2(g)} \rightarrow Pd_2(CO)_2Cl_{4(g)} \qquad (1d)$$

$$Pd_2(CO)_2Cl_{4(g)} \rightarrow Pd_2(CO)_2Cl_{4(s)} \qquad (1e)$$

$$Pd_2(CO)_2Cl_{4(s)} \rightleftarrows Pd_2(CO)_2Cl_{4(SOCl_2)} \qquad (1f)$$

The measured thermodynamic parameters can be used to gain some information about the strength of the palladium–CO bond (eq 1c). In order to do so, some assumptions have to be made. Palladium(II) chloride exists in two crystalline modifications: the α form[10] is a polymeric chain of planar $PdCl_4$ units containing bridging chlorides (Cl_{br}) only, while the β form, similar to the corresponding platinum(II) derivative,[11] is a hexamer Pd_6Cl_{12} consisting[12a] of a palladium octahedron with bridging chlorides. A new method of preparation of β-$PdCl_2$ has appeared, and a third form of the chloride probably exists.[12b] An entropy change of about −31 eu is associated with the loss of translational and vibrational motions of CO to form the dimeric chloro carbonyl complex[1] and with the reorganization of the solvent around the reaction product, which are not compensated by the disruption of the polymeric structure of $PdCl_{2(s)}$. A detailed examination of the enthalpy contributions requires an evaluation of the (1a)–(1f) contributions. For (1a) the enthalpy change was calculated[13] to be +68 kcal/mol. This is the basis for the accepted[12a] mean bond energies of Pd–Cl_{br} (48 kcal) and Pd–Cl_t (62 kcal), with Cl_t standing for terminal chloride. The formation of $PdCl_{2(g)}$ from $PdCl_{2(s)}$ requires the rupture of two Pd–Cl_{br} bonds per mole of $PdCl_2$ and the reorganization of two Pd–Cl_{br} bonds to the same number of Pd–Cl_t bonds. For (1b) our experimental data and the corresponding plot of $-\ln X_2$ vs. $1/T$ (see Table I and ref 8) show that the enthalpy change for the solvation of CO from the gas phase is close to zero. For (1d) the enthalpy change for the dimerization of $PdCl_{2(g)}$ to the corresponding chloride-bridged dimer in the gas phase can be calculated to be −68 kcal/mol of dimer, since the formation of the latter corresponds to the cleavage of two Pd–Cl_t bonds and the formation of four new Pd–Cl_{br} bonds. For (1e) the heat corresponding to this process can be taken to be the same as that assumed[14] for $Rh_2(CO)_4Cl_2$, namely −38 kcal/mol. We realize that this could be an upper value for the palladium dimer since the rhodium(I) complex was shown[15] to have metal–metal interactions in the solid state, a feature that, although equally possible for $Pd_2(CO)_2Cl_4$, has not been proved as yet. For (1f) our measurements of the solubility equilibrium of $Pd_2(CO)_2Cl_4$ (see Table I) gave a value of +5.8 kcal for the heat of solution. It is interesting to note that the calorimetric determination of the heat of solution of the palladium(II) complex $Pd(PhCN)_2Cl_2$ in dichloromethane gave[16] a value of $+8.43 \pm 0.19$ kcal. Thus, insertion of the corresponding values in the thermodynamic sequence (1a)–(1f) led to a value of about 24 kcal for the Pd–CO bond energy. This, of course, assumes that the Pd–Cl bond strength of anhydrous palladium(II) chloride remains unchanged in the carbonyl derivative. Under this assumption, the calculated value compares well with the Fe–CO bond energies of 15.3 and 17.5 kcal calculated[14] for $Fe(CO)_4Br_2$ and $Fe(CO)_4I_2$, respectively, considering that the strength of metal–CO bonds normally increases from 3d to 4d elements.[14] Average metal–CO bond strengths for zerovalent metal carbonyls range from 24 kcal for $Mn_2(CO)_{10}$ to 35 kcal for $Ni(CO)_4$, while for 4d metals the range is from 36.3 kcal for $Mo(CO)_6$ to 41.1 kcal for $Ru_3(CO)_{12}$.[14] It is interesting to note that an estimate[14] of the Pd–CO bond energy is about 25 kcal. The agreement with our value is more impressive than real, since we are dealing with different oxidation states of the metal.

The experimentally established exothermicity of reaction 1 and the thermodynamic parameters derived from it do not appear to lend support to the hypothesis that the Pd–CO bond is a particularly weak one, at least as far as the oxidation state II is concerned. On the other hand, the presumably low, if any, π contribution to the Pd–CO bond[1] increases the polarity of the bond and therefore its reactivity toward nucleophiles. The low availability of d orbitals for π back-bonding with metals at the end of the periodic table[17] could alter the usual trend to an increase of the M–CO bond strength by decreasing the oxidation state of the metal, and at the same time, σ donation would be less favored. In conclusion, for palladium and perhaps some other metals in its vicinity, the strength of the metal–CO bond could change anomalously with respect to transition metals with a lower d^n electron configuration.

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This could explain the nonexistence of $Pd(CO)_4$ and its alleged thermodynamic instability with respect to $Pd_{(s)} + 4CO$, in spite of the lower heat of sublimation[18] of palladium (91 kcal/mol) as compared to that of nickel (102.8 kcal/mol). It can be tentatively suggested that the frequent use of Lewis-acid cocatalysts in carbonylation reactions promoted by palladium[19] might be related to their electron-withdrawing power, which could make a lower energy path for the chemisorption or the coordination of CO.

Concerning the palladium(I) carbonyl complex reported in this paper, it was obtained by reduction of $PdCl_2$ with CO in acetic anhydride at room temperature. Under these conditions, no further reduction was observed and excellent yields of $[Pd(CO)Cl]_n$ were secured. In view of the fact that CO was consumed when the compound was prepared from $Pd_2(CO)_2Cl_4$ or from $PdCl_2$, it is assumed that the reduction is carried out by CO itself, according to the stoichiometry of eq 4 for $Pd_2(CO)_2Cl_4$ and eq 5 for $PdCl_2$. Some CO_2 was found

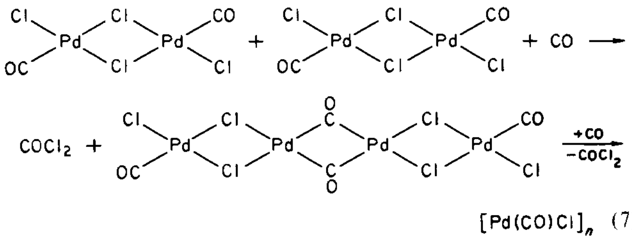
$$0.5Pd_2(CO)_2Cl_4 + 0.5CO \xrightarrow{Ac_2O} (1/n)[Pd(CO)Cl]_n + 0.5COCl_2 \quad (4)$$

$$PdCl_2 + 1.5CO \xrightarrow{Ac_2O} (1/n)[Pd(CO)Cl]_n + 0.5COCl_2 \quad (5)$$

in the reaction mixture, presumably due to the slow reaction (6) with acetic anhydride.[20]

$$(AcO)_2O + COCl_2 \rightarrow 2AcCl + CO_2 \quad (6)$$

In agreement with earlier results[3] we also find that the presumably polymeric palladium(I) carbonyl complex forms the carbonyl-bridged[21] $[Pd_2(CO)_2Cl_4]^{2-}$ anion, showing a main carbonyl absorption at 1916 cm^{-1}. The carbonyl chloro complex of palladium(I) was suggested[3c] to have a polymeric structure containing alternating chloride and CO bridges. The formation of such a structure can be visualized to occur through the polymerization of $Pd_2(CO)_2Cl_4$, via $COCl_2$ elimination, a process that has been observed earlier in these laboratories with gold(III) to produce $Au(CO)Cl$[17c] and with platinum(IV) to produce $Pt(CO)_2Cl_2$:[17b]



(7)

We believe that the band of low intensity we observe at about 2170 cm^{-1} is due to some palladium(II)-terminated oligomers.

To conclude, this work has indicated that the palladium(II)–CO bond is probably characterized by a substantially "normal" strength. On the other hand, π back-bonding is unessential[1] for stabilizing *terminal* Pd(II)–CO bonds, presumably due to the much too low energy of the palladium d electrons. If the σ mechanism is the only one to operate, ***terminal Pd–CO bonds are expected to be weaker as the oxidation state of the metal decreases***, contrary to the situation encountered with many transition elements. $Pd(CO)_4$ would then be intrinsically unstable with respect to the metal. Consistent with this picture are the following observations: (a) Palladium(I) of d^9 configuration has bridging[21] CO's in $[Pd_2(CO)_2Cl_4]^{2-}$ and possibly in $[Pd(CO)Cl]_n$, as discussed above. On a first approximation this may be understood by considering that the μ-Cl situation would correspond to a 18-valence-electron counting, an uneasy one to accommodate terminal Pd–CO bonds. The 16-valence-electron situation with bridging CO's is therefore preferred. (b) Chemisorption of CO on palladium mainly gives CO-bridged structures.[22]

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Registry No. 1, 75991-68-3; $[NH_2Et_2]_2[Pd_2(CO)_2Cl_4]$, 87901-25-5; $[Pd(CO)Cl]_n$, 28551-87-3; $PdCl_2$, 7647-10-1; $SOCl_2$, 7719-09-7.

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