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Kinetics and Thermodynamics of the Reversible Reaction between Carbon Monoxide and Palladium(I) Dimers Containing Bis(diphenylphosphino)methane

Chung-Li Lee,[1a] Brian R. James,*[1a] David A. Nelson,*[1b] and Richard T. Hallen[1b]

Chemistry Department, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6, and Pacific Northwest Laboratory, Richland, Washington 99352

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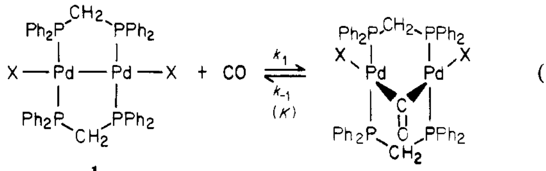
The kinetic and thermodynamic parameters for the reversible insertion of carbon monoxide into the palladium–palladium bond of $Pd_2(dpm)_2X_2$ complexes (dpm = $Ph_2PCH_2PPh_2$; X = Cl, Br, I, NCO) in *N,N'*-dimethylacetamide solution have been determined by spectrophotometric methods. The forward reaction is first order in both Pd_2 and CO and occurs on the stopped-flow time scale at around ambient temperatures, the rate constants being similar for the four systems $(3.15–6.60) \times 10^3$ M^{-1} s^{-1} at 24 °C. The equilibrium constants, estimated by kinetic and/or static methods, decrease in the order X = NCO > Cl > Br > I (from 3.7×10^5 to 1.3×10^3 M^{-1} at 24 °C) and are governed largely by the first-order off-rates, which probably depend more on a weakening of the Pd–CO bonds throughout the series than changes in the metal–metal bond strength. A correlation between ln k_{-1} for the off-rates and the energy of a high intensity UV band of the $Pd_2(dpm)_2X_2$ complexes is noted. The CO addition to give $Pd_2(dpm)_2(\mu\text{-CO})X_2$ occurs because of the exothermicity of the reaction that is unfavorable in terms of ΔS; an approximate value of 90–120 kJ mol^{-1} is estimated for the Pd–Pd bond strength. The systems show high selectivity for binding of CO in the presence of H_2, C_2H_2, C_2H_4, CO_2, O_2, or air.

Introduction

Recently, interest has intensified in the separation of components from coal gasification streams. Cyrogenic and membrane separation techniques have been considered;[2,3] however, the former is energy intensive while the latter has not been fully developed. Use of transition-metal complexes that are known to reversibly bind gas molecules offers a further plausible procedure for separating gaseous components. Such a procedure has been studied in detail for separation of O_2 from air using several complexes, particularly cobalt(II) Schiff base[4,5] and manganese(II) phosphine systems,[6] and a variety of transition-metal hydride systems have attractive properties for separation and storage of H_2.[7–9] We have focussed attention on selective reversible binding of CO. The number of transition-metal complexes that bind CO reversibly is vast and includes, for example, Vaska-type complexes and related platinum metal d^8 systems,[10,11] metalloporphyrin, metalloenzyme, and related protein model complexes (usually of Fe and Cu),[12–15] as well as binary metal carbonyls themselves such as $Rh_4(CO)_{12}$.[16] Most of these systems are nonselective, however, and typically react with (are poisoned by) O_2, H_2, moisture, etc. Some air-stable, bis(amine)(phthalocyanato)iron(II) systems studied some years ago in one of our laboratories[17] showed the desired selectivity, but the systems formed the amine carbonyl in a two-stage process via initial dissociation of an amine ligand. A more simple reversible addition of CO, not involving a substitution process, has been reported by Balch and co-workers[18] for palladium(I) A-frame dpm[19] complexes (eq 1, X = anion).



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These systems seemed of interest as potential selective binding reagents for CO, and we decided to study the kinetics and equilibria of process 1, initially in solution. Reaction 1 presents a relatively rare case when the carbonyl of the product bridges metal atoms not joined by a metal–metal bond, and determination of the thermodynamic parameters for such equilibria seemed to allow also for an indirect probe into the strength of the metal–metal bond.

Experimental Section

General Data. The primary palladium source was $PdCl_2$ (Strem). The dpm ligand (Strem) and the gases (Matheson C.P. grade CO, H_2, C_2H_4, C_2H_2, CO_2) were used without further purification. The $Pd_2(dpm)_2Cl_2$ complex was synthesized from $Pd(PhCN)_2Cl_2$, $Pd_2(dba)_3\cdot CHCl_3$, and dpm, and the $Pd_2(dpm)_2X_2$ (X = Br, I, NCO) complexes were synthesized from the chloride precursor, by the published methods.[18] Dichloromethane (Fisher) was distilled prior to use, while dma (Eastman Kodak) was purified by storing over CaH_2 under N_2 for long periods followed by

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[19] Abbreviations used: dpm = bis(diphenylphosphino)methane; dba = dibenzylideneacetone; dma = *N,N'*-dimethylacetamide; dam = bis(diphenylarsino)methane.

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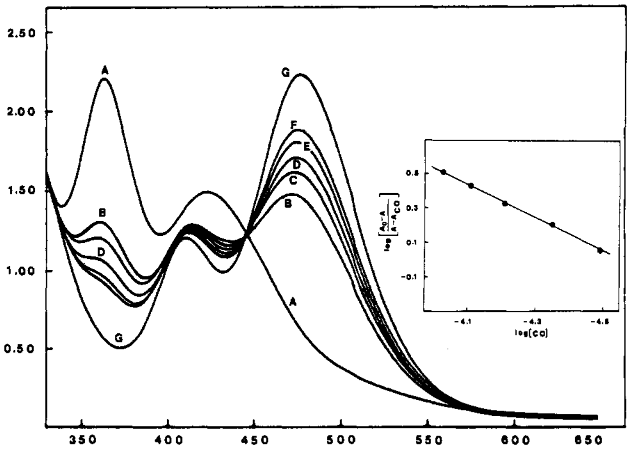

Figure 1. Spectrophotometric titration of $Pd_2(dpm)_2Br_2$ with CO in dma at 24 °C: A, 100% $Pd_2(dpm)_2Br_2$; G, 100% $Pd_2(dpm)_2(\mu\text{-}CO)Br_2$ at 760 torr of CO; spectra B to F measured in presence of 5.45, 7.8, 10.6, 13.3, and 16.0 torr of CO, respectively. Insert shows plot according to eq 2.

distillation under reduced pressure.

The stoichiometry of reaction 1, and the solubility of CO in dma, were measured with the constant-pressure apparatus described elsewhere.[20]

Kinetic Measurements. The faster reactions with $t_{1/2} < 5$ min were studied by using a thermostated Durrum 110 stopped-flow apparatus equipped with a 2-cm light path cuvette. The average k_{obsd} values were determined by monitoring absorption of the reactant or the carbonyl at their respective λ_{max} values (see Figure 1); measurements were made at two wavelengths by using a minimum of three experiments. Conditions were chosen so that reactions followed the first-order rate law $\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_{obsd}t$, where A_0, A_t and A_∞ are the solution absorbances at $t = 0$, time t, and completion of the reaction, respectively. A linear regression analysis was used to obtain k_{obsd} from the $\ln(A_t - A_\infty)$ vs. t plot; the plots were linear over at least 3 half-lives and the precision obtained was always better than 10% over the 0–40 °C temperature range used.

The $[Pd_2]$ was varied from 0.33 to 1.75×10^{-4} M, while a concentration range in CO was made available by varying the partial pressures of CO and Ar in a total of 1 atm at 25 °C. The effect of other added gases on the carbonylation rates was examined by using gas mixtures with known partial pressures. The solubility of CO in dma was 4.4×10^{-3} M atm^{-1} at 24 °C (Henry's law being obeyed) and was about 2% lower at 40 °C and 2% higher at 0 °C. In the mixing chamber of the stopped-flow instrument, equal volumes of the Pd and gas solutions are mixed; thus the actual concentration of gas in the reaction solution is half that made up and transferred to the storage syringe.

Slower reaction rates, usually the decarbonylation (k_{-1}), were measured in a thermostated Perkin-Elmer 552A spectrophotometer using a specially designed cell consisting of a 1-cm path length cell attached by a side arm to a reservoir bulb, and fitted with a Teflon stopcock and an O-ring joint for attachment to a vacuum/gas-handling line.[17] A solution of 2, formed in situ via the carbonylation reaction, was exposed to vacuum with vigorous shaking prior to monitoring the absorbance (loss of solvent during several evacuations was taken into account). The standard log (absorbance difference) vs. time plots (see above) gave linearity over several half-lives from which the first-order rate constant k_{-1} was readily evaluated.

Equilibrium Constant Measurements. Samples of 1 (to give ~1.5×10^{-4} M solutions) were weighed into the special cell described above, with 5 mL of dma being present in the reservoir bulb. Following degassing by several freeze–pump–thaw cycles, the dma was transferred to dissolve 1 and the apparatus then filled to 1 atm pressure with CO/Ar mixtures in which the CO partial pressure could be varied from 0 to 760 torr at the required temperatures between 0 and 40 °C. The solution was then shaken to establish the equilibrium shown in eq 1, and the UV/vis spectrum recorded in the thermostated Perkin-Elmer 552A. The procedure was repeated at varying CO pressures at several temperatures. Corrections for the vapor pressure of dma were negligible (1.0 torr at 15 °C, 4.5 torr at 40 °C[21]). Pressures of CO were chosen to give a reasonable variation in [2]/[1], as well as complete formation of 2; excellent isosbestics were observed at any given temperature (see Figure 1).

The analysis for equilibrium 1 is standard by using the expressions shown in (2) at any convenient wavelength, where A_0

$$K = [2]/[1][CO]$$

$$\log\left[\frac{A_0 - A}{A - A_{CO}}\right] = \log K + \log\,[CO] \tag{2}$$

and A_{CO} are the absorbance of $Pd_2(dpm)_2X_2$ (1) and $Pd_2(dpm)_2(CO)X_2$ (2), respectively; A is the absorbance at some known CO pressure (concentration) when mixtures of 1 and 2 are present. For the X = Cl, Br, and NCO systems, plots of $\log[(A_0 - A)/(A - A_{CO})]$ vs. log [CO] were linear with slope 1.0 ± 0.10 confirming the 1:1 stoichiometry (see Figure 1); the plots were fitted with a linear regression program to determine K (±10%). For the iodide system, the carbonyl was not quite fully formed at up to 2 atm of CO pressure, and A_{CO} could not be determined directly (see below).

Results and Discussion

The UV/vis spectra of the $Pd_2(dpm)_2X_2$ (X = Cl, Br, I, NCO) complexes 1 in CH_2Cl_2 were the same within experimental error of those reported;[18] the spectra in dma solution were identical. Exposure of the orange solutions of 1 to CO rapidly resulted in a darkening of the color and a red-shift of the absorption maxima (Figure 1); the product solutions 2 showed two maxima; one around 400–425 nm and a more intense one in the 440–500-nm region depending on X. Balch's group[18] reported only relative absorbance values for the maxima of the carbonyls; our values are in excellent agreement and the fully formed in situ species yield the following extinction coefficients (M^{-1} cm^{-1}) for the major peak: X = Cl, 13 400 at 468 nm; X = Br, 16 000 at 480 nm; X = I, ~16 000 at 500 nm (see below); X = NCO, 15 600 at 445 nm.

The $Pd_2(dpm)_2X_2$ complexes are well characterized;[18,22] the carbonyls, formed by direct insertion into the Pd–Pd bond, are characterized by spectroscopy and by analogy to the diarsino complex $Pd_2(dam)_2(\mu\text{-}CO)Cl_2$ of known structure.[23] We further confirmed the 1:1 stoichiometry by CO absorption by dma solutions of $Pd_2(dpm)_2Cl_2$ at 25 °C. Decarbonylation was accomplished by purging the solutions with Ar or by exposure to vacuum.

The rate law for process 1 is a standard one given in eq 3, and an integrated form is given in eq 4.[24]

$$\frac{-d[1]}{dt} = \frac{d[2]}{dt} = k_1[1][CO] - k_{-1}[2] \tag{3}$$

$$\ln\left[\frac{A_0 - A_\infty}{A_t - A_\infty}\right] = (k_1[CO] + k_{-1})t \tag{4}$$

Under the stopped-flow conditions the [CO] is effectively constant and the observed first-order rate constant k_{obsd} equals $(k_1' + k_{-1})$ where $k_1' = k_1[CO]$. The k_{obsd} values at a fixed [CO] were independent of the initial $[Pd_2]$, con-

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Table I. Thermodynamic and Kinetic Data for the Reaction of $Pd_2(dpm)_2X_2$ with CO in dma Solution[a]

X	$10^{-4}K$,[b] M^{-1}	$P_{1/2}$, torr	$10^{-3}k_1$, $M^{-1}\ s^{-1}$	k_{-1},[c] s^{-1}	ΔH,[d] kJ mol^{-1}	ΔS,[d] J mol^{-1} K^{-1}	$\Delta H_1^{\ddagger}$,[e] kJ mol^{-1}	$\Delta S_1^{\ddagger}$,[e] J mol^{-1} K^{-1}	$\Delta H_{-1}^{\ddagger}$,[f] kJ mol^{-1}	$\Delta S_{-1}^{\ddagger}$,[g] J mol^{-1} K^{-1}
NCO	37	0.47	3.15	8.5×10^{-3}	−48	−55	26	−92	74	−38
Cl	24	0.71	6.6	2.7×10^{-2}	−57	−85	15	−120	72	−34
Br	3.5	4.9	6.0	0.17	−61	−113	15	−121	76	−8
I	0.13	130	4.2	3.2	−48	−100	23	−100	71	0

[a] Equilibrium and rate constants are values at 24 °C. [b] Measured by static method (eq 2), except for X = I when stopped-flow kinetic data were used (Figure 3). [c] Estimated from k_1/K; directly measured values at 24 °C were (s^{-1}) 9.0×10^{-3} (NCO), 1.4×10^{-2} (Cl), and 3.8×10^{-2} (Br). [d] Values of ΔH and ΔS were obtained from a least-squares analysis of the data points; errors are estimated to be ±6 kJ mol^{-1} and ±20 J mol^{-1} K^{-1}. [e] Arrhenius $\Delta E^{\ddagger}$ measured from stopped-flow data (4–24 °C); $\Delta H^{\ddagger} = \Delta E^{\ddagger} - RT$, $T = 297$ °K; errors ±3 kJ mol^{-1} ($\Delta H_1^{\ddagger}$) and ±10 J mol^{-1} K^{-1} ($\Delta S_1^{\ddagger}$). [f] Estimated from $-\Delta H + \Delta H_1^{\ddagger}$, except for the direct measurement for the iodo system (Figure 3); an experimental value from limited stopped-flow data for the bromo system (cf. Figure 3) was ~60 kJ mol^{-1}! [g] Estimated from $\Delta S_1^{\ddagger} - \Delta S$.

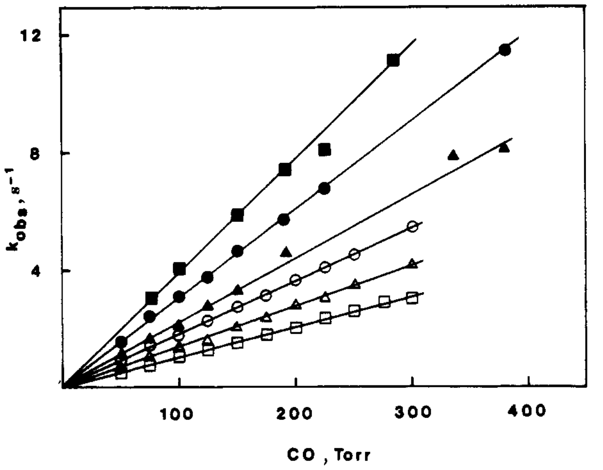


Figure 2. Plots of k_{obsd} vs. [CO] (given as partial pressure) for reaction of CO with $Pd_2(dpm)_2Cl_2$ (■, 24 °C, ● 16 °C, ▲, 4 °C) and with $Pd_2(dpm)_2(NCO)_2$ (○, 24 °C, △, 16 °C, □, 10 °C) in dma.

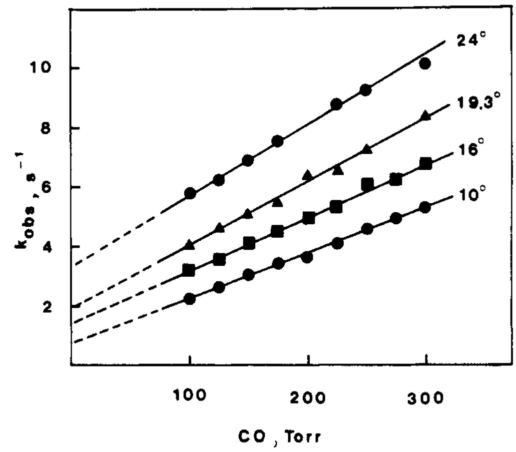


Figure 3. Plots of k_{obsd} vs. [CO] (given as partial pressure) for reaction of CO with $Pd_2(dpm)_2I_2$ in dma at several temperatures.

firming the first-order dependence on $[Pd_2]$. Plots of k_{obsd} vs. [CO] are linear (Figures 2 and 3), thus showing the first-order dependence on [CO], the slope of the line yielding k_1; data at lower temperatures (4–24 °C) for the X = Cl, Br, and NCO systems are typified by those in Figure 2. That the plots go through the origin implies that k_{-1} (the intercept) is negligible on the scale used for k_{obsd}. For the iodide system (Figure 3) and the bromide system at higher temperatures (45–55 °C), k_{-1} may be evaluated at least approximately as a measurable intercept, as well as k_1; thus the equilibrium constant K is determined indirectly as the k_1/k_{-1} ratio. All the kinetic and thermodynamic parameters listed in Table I for the iodide system were evaluated from the stopped-flow data alone; excellent Arrhenius and Van't Hoff plots were obtained. The stopped-flow k_1 data for the chloro, bromo, and cyanato systems also gave excellent Arrhenius plots.

Figure 1 shows a typical equilibrium plot according to eq 2, and the thermodynamic parameters listed for the X = Cl, Br, and NCO systems (Table I) were determined again from excellent Van't Hoff plots. For the bromo system, values for K at lower temperatures, determined by using eq 2 and electronic spectral data, were very compatible with values measured at the higher temperature by the stopped-flow k_1/k_{-1} data (Figure 4). The k_{-1} values for these three systems could be estimated from the ratio of k_1/K or measured directly (see Experimental Section). The agreement between such k_{-1} values for the carbonyl cyanato complex, which gave the lowest "off-rate", was excellent, but as the decarbonylation rates increased (with $t_{1/2} \leq 25$ s at 24 °C as judged from the k_1/K values), the discrepancy between the sets of k_{-1} values became greater. The technique used for decarbonylation (evacuation/shaking) was clearly not efficient enough to remove the CO, or, in other words, there is at least partial diffusion control of CO loss from the solution. The k_{-1} values calculated from k_1/K are considered correct, and the $\Delta H_{-1}^{\ddagger}$ values listed in Table I were thus estimated from $(-\Delta H + \Delta H_1^{\ddagger})$ for these exothermic reactions. For the bromo and iodo systems, $\Delta H_{-1}^{\ddagger}$ values were also determined directly from Arrhenius plots for the intercept k_{-1} values estimated from the stopped-flow data (see Figure 3).

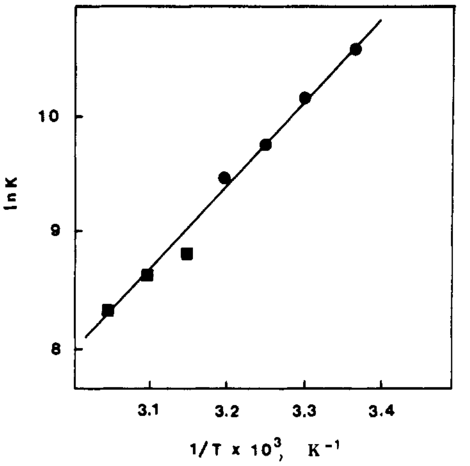
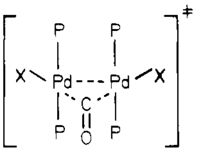


Figure 4. Dependence of equilibrium constant on temperature for reaction of CO with $Pd_2(dpm)_2Br_2$: ●, data from static method (eq 2) at 24–40 °C; ■, data from stopped-flow at 44–55 °C.

Some stopped-flow experiments for the carbonylation of $Pd_2(dpm)_2Cl_2$ at 150 torr and 24 °C (Figure 2) were modified in that other gases at a partial pressure of 280 torr were added also: the k_{obsd} values in the presence of Ar, H_2, C_2H_2, C_2H_4, CO_2, O_2, or air were 5.4 ± 0.1 s^{-1}, compared to a value of 5.8 s^{-1} with just pure CO. At 100 torr of CO (k_{obsd} = 4.0 s^{-1}), addition of 280 torr of Ar, 280 torr of C_2H_4, or a 280 torr 1:1 mixture of Ar/C_2H_4, resulted in a measured k_{obsd} value of 3.2 s^{-1} in each case. The conclusion is that the system shows very high selectivity for CO binding in the presence of these gases. The somewhat lower rate constants in the presence of other gases is almost certainly due to a somewhat lower solubility of the CO.[25] There was, of course, no reactivity of the chloro dimer toward any of the above gases alone at 760 torr. The $Pd_2(dpm)_2X_2$ complexes are, however, known to bind SO_2 reversibly by insertion into the Pd–Pd bond[22] and to react with activated acetylenes to yield cis dimetalated olefinic species also having no metal–metal bond.[26]

Addition of chloride (Cl^-:Pd_2 = 40) had no effect on the k_1 value for the $Pd_2(dpm)_2Cl_2$ carbonylation, which is consistent with the one-stage concerted process shown in eq 1 with no involvement, for example, of halide dissociation. Addition of dpm to a solution of $Pd_2(dpm)_2Cl_2$ caused decomposition to $Pd(dpm)Cl_2$ (detected by ^1H and ^{31}P NMR[27]) and other unidentified complexes, and so any possible kinetic/mechanistic role for the diphosphine ligand (e.g., dissociation at one end) remained undetectable; monodentate dpm complexes are known.[28] It seems unnecessary to invoke such pathways, however, and a simple transition state such as **3** is strongly favored.



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The kinetic and thermodynamic enthalpy and entropy parameters, together with selected rate and equilibrium constants, are given in Table I. The $P_{1/2}$ values are the pressures required for 50% carbonylation and are simply the inverse of K expressed as $torr^{-1}$. Since the ratio of carbonylated species to starting complex present ([**2**]:[**1**]) is given by (CO partial pressure/$P_{1/2}$), it is seen that carbonylation is essentially complete at relatively low pressures for the X = NCO and Cl systems, the **2**:**1** ratio being 50 at about 23 and 36 torr, respectively. The corresponding ratio is reached at about 245 torr for the bromo dimer, while for the iodo complex the ratio is only about 5.75:1 even at 1 atm (and 11.5:1 at 2 atm). The "on-rates" (k_1) for all four systems are fast and within a factor of about 2; even at the lowest temperature studied (4 °C) with about 50 torr of CO, half-lives are of the order of a second. The carbonylation are fast because of the quite low activation enthalpies ($\Delta H_1^{\ddagger}$) required; indeed, the $\Delta H_1^{\ddagger}$ values are among the lowest reported for addition of gases to metal centers and are similar, for example, to those measured for binding of CO (and O_2) to myoglobin and protein-free models.[12,13] The myoglobin and model reactions are even faster, however, ($k_1 \approx 10^5$–10^7 M^{-1} s^{-1} at 25 °C) because the $\Delta S_1^{\ddagger}$ values are considerably less negative than those measured for the Pd dimers (Table I); the steric requirements for fixing the gas between two metal centers in a transition state such as **3** must be severe.

The equilibrium constants decrease in the order X = NCO > Cl > Br > I, in complete agreement with a qualitative trend noted by Balch and co-workers;[18] the order is clearly governed by the off-rates (k_{-1}) that decrease in the reverse order (I > Br > Cl > NCO). Assuming that the structure of the carbonyls are analogous to that of $Pd_2(dam)_2(\mu\text{-}CO)Cl_2$,[23] the X ligands are trans to the bridging carbonyl (see **2**), and the order corresponds to their trans effects.[29] Balch and co-workers surmised that the higher trans effect would give a weaker metal–metal bond in complexes such as **1** but also a weaker metal–carbonyl bond in **2** and that the latter effect must be predominate.[18] Our data show that there is no correlation of the CO lability with the ν(CO) stretch of the complexes (Cl, 1705, Br, 1712, I, 1713, NCO, 1720 cm^{-1}),[18] but this is not unusual.[30] Indeed, the variation in k_{-1} values, which decrease by a factor of 400 on going from the iodo to cyanato system, is generally reflected largely by differences in $\Delta S_{-1}^{\ddagger}$. The transition state must be something akin to **3** with approximate trigonal-bipyramidal geometry at each Pd; in the reverse reaction continued formation of the metal–metal bond eventually forces out the CO to leave essentially square-planar coordination at each Pd.[23] The relatively small values of $\Delta S_{-1}^{\ddagger}$ are reasonable for a unimolecular reaction such as this requiring little rearrangement to form the transition state. The forward reaction, involving fixing the free (solvated) gas molecule at metal centers, shows the expected unfavorable entropy of reaction as well as entropy of activation. The findings here on relative ΔS, $\Delta S^{\ddagger}$, and $\Delta S_{-1}^{\ddagger}$ values appear to be quite general for reversible binding of CO[10,12] (to give a terminal M–CO species) and also for reversible binding of H_2[31] and O_2.[12,13] To the best of our knowledge, all solution reactions involving simple coordinative addition of a gas molecule give substantially negative ΔS values, and the property of the binding results from the exothermicity of the process. This is seen again in Table I. All the experimental data are consistent with the formulation of the product as shown, **2**; there is no dissociation of halide to give an ionic product that has been observed with corresponding platinum systems in methanol solution.[32]

The exothermicity, ignoring solvation effects, is roughly a measure of the difference between the two Pd-bridged CO bond strengths in the dimetallic ketone product and the Pd–Pd bond strength in the precursor A-frame complex. Knowledge of either allows for an estimation of the other. a bond energy for Pd-*terminal* carbonyls (Pd–CO_t) in the chloro-bridged palladium(II) complex $[Pd(CO)Cl]_2(\mu\text{-}Cl)_2$ has been determined recently[33] as ~100 kJ mol^{-1}, while an estimate in a zerovalent species[34] is ~105 kJ mol^{-1}. On the basis of these data, a similar value will be assumed for a Pd(I) species. A bridged M–CO_{br} bond energy is commonly 50–75% that of M–CO_t, although these data are for bridging carbonyls that span metal–metal bonded systems.[34-36] [It is also worth noting that the bond energy for Pd^{II}–Cl_{br} (200 kJ) is also ~75% that

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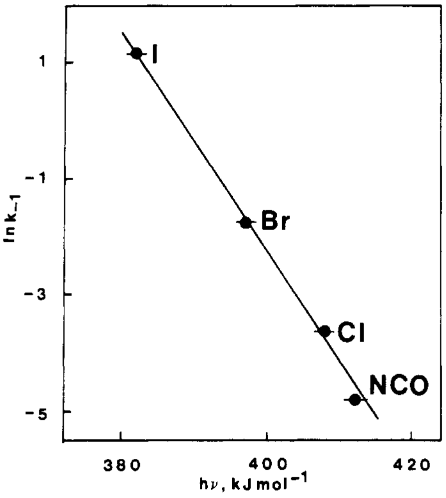

Figure 5. Correlation between ln k_{-1} values at 24 °C and a high intensity UV band of the $Pd_2(dpm)_2X_2$ complexes.

of Pd^{II}–Cl_t (260 kJ).[37]] Following this tenuous thread, a crude estimate of ~75 kJ mol^{-1} may be taken for the Pd–CO_{br} bond energy in **2**, this estimate necessarily including changes in the weakening of the CO bond on coordination. Using the ΔH values given in Table I then yields a Pd–Pd bond strength of ~90–120 kJ mol^{-1}. A more reliable estimate of this bond strength must await a better number for the Pd–CO_{br} bond energy. Nevertheless, the data do indicate a relatively weak Pd–Pd bond,[34,35] which is consistent with the unusually long metal–metal bond found in this type of A-frame complex (at least within $Pd_2(dpm)_2Br_2$, 2.699 Å[38]) compared with other Pd_2^I complexes;[38] this presumably reflects accommodation of the dpm ligand.

It is worth noting that, as well as the absorption bands in the visible region of the spectrum (see above and Figure 1), the $Pd_2(dpm)_2X_2$ complexes exhibit two strong absorptions in the UV,[18] and a reasonable correlation exists between the ln k_{-1} values at 24 °C and the energy of the most intense and higher energy band (NCO, 290 nm; Cl, 293 nm; Br, 301 nm; I, 313 nm) (Figure 5). The qualitative arguments noted above imply that the cyanate system is expected to have the strongest Pd–CO_{br} and Pd–Pd bonds, with the former being more important within equilibrium 1; thus the noted correlation is not consistent with the UV band chosen arising from a metal–metal $\sigma \rightarrow \sigma^*$ transition, and the band probably reflects some metal $d\pi \rightarrow \pi^*$ (ligand) charge-transfer process. However, such a conclusion is extremely tentative; studies on the band assignments for complexes **1** and **2** are needed before kinetic–spectroscopic correlations can be discussed meaningfully. Further, in such cases, differences in the absorption band energies are usually discussed in terms of contributions to the enthalpy of activation;[39] differences in k_{-1} values in the present system appear to arise largely from differences in the entropies of activation.

Finally, one comment should be made concerning the suitability of these complexes in solution for removing CO from gas streams. From both kinetic and thermodynamic viewpoints, the systems are promising and, indeed, the rapid rates imply that both the on- and off-rates within a working system would be governed totally or in part by diffusion control from the gas to liquid phase (or vice-versa) and more likely to be determined by engineering design rather than chemical rates. Ongoing studies involve attaching complexes such as **1** chemically to a support via the methylene group of the dpm ligand.

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Registry No. **1** (X = Cl), 64345-29-5; **1** (X = Br), 60482-68-0; **1** (X = I), 67477-87-6; **1** (X = NCO), 68079-57-2; **2** (X = Cl), 64345-32-0; **2** (X = Br), 64345-33-1; **2** (X = I), 90433-53-7; **2** (X = NCO), 68079-42-5; Pd, 7440-05-3; CO, 630-08-0.

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