Spectroscopic Studies on Matrix-isolated Metal Carbonyls. Part II.[1] Infrared Spectra and Structures of $Pd(CO)_4$, $Pd(CO)_3$, $Pd(CO)_2$, and PdCO

By **J. H. Darling** and **J. S. Ogden,*** Inorganic Chemistry Laboratory, South Parks Road, Oxford

The co-condensation of palladium atoms with carbon monoxide in inert matrices at low temperatures leads to the formation of binary palladium carbonyls. This paper describes the characterisation of these using i.r. spectroscopy, and with the aid of $C^{18}O$ isotope enrichment, the four most prominent species are shown to be $Pd(CO)_4$ T_d, $Pd(CO)_3$ D_{3h}, $Pd(CO)_2$ $D_{\infty h}$, and PdCO. Diffusion studies indicate that the lower carbonyls readily react with excess CO to yield $Pd(CO)_4$, and that this species is stable in a xenon matrix up to *ca.* 80 K. The appropriate principal and interaction carbonyl force constants are evaluated for all four species, and an estimate is also obtained for the palladium–carbon stretching force constant in $Pd(CO)_4$.

SEVERAL papers have recently appeared [2-8] describing the synthesis of new binary carbonyls using matrix isolation techniques, and in particular, two independent groups have reported that palladium tetracarbonyl is a product of the co-condensation of palladium atoms and carbon monoxide in low temperature matrices. This species was initially detected by i.r. spectroscopy,[7,8] and subsequently also by Raman spectroscopy,[9] and has been shown to be tetrahedral by $C^{18}O$ enrichment studies[8] and by polarisation data.[9] A number of other palladium carbonyls were also detected in these preliminary experiments but were not characterised, although by analogy with DeKock's matrix isolation synthesis of nickel carbonyls,[2] it was suggested that they might be the lower carbonyls $Pd(CO)_3$, $Pd(CO)_2$, and PdCO.

The first paper in this series [1] shows how the use of $C^{18}O$ enrichment in the matrix isolation synthesis of binary carbonyls allows one to identify new molecules on the basis of characteristic i.r. frequency and intensity patterns. This paper describes in detail the results obtained in our matrix isolation synthesis of palladium carbonyls over a wide range of experimental conditions.

EXPERIMENTAL

The Knudsen furnace and low temperature cryotip used for our matrix isolation studies have been described previously.[10] In these experiments, palladium wire (99·99%) was heated to *ca.* 1800 K in zirconia or alumina sample holders and the vapour, which is predominantly monatomic,[11] was deposited on a cooled CsI window with an excess of inert matrix containing a few mol per cent of carbon monoxide. Research grade matrix gases (grade ' X ' Ar, Kr, or Xe) and $C^{16}O$ were obtained from the British Oxygen Co. and ^{18}O enriched carbon monoxide (92% $C^{18}O$) was supplied by Miles Laboratories Inc. The proportion of carbon monoxide in the matrix gas was varied from 0·1 to 10%, and gas samples were accurately made up by using a Toepler pump which ensured complete mixing. Matrix deposition rates were kept constant at *ca.* 5 mmol h^{-1}, and the matrix ratio was estimated to be *ca.* 1000 : 1. The

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[1] Part I, J. H. Darling and J. S. Ogden, *J.C.S. Dalton*, 1972, 2496.

[2] R. L. DeKock, *Inorg. Chem.*, 1971, **10**, 1205.

[3] J. L. Slater, R. K. Sheline, K. C. Lin, and W. Weltner, jun., *J. Chem. Phys.*, 1971, **55**, 5129.

[4] A. Bos, *J.C.S. Chem. Comm.*, 1972, 26.

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[6] A. J. Hinchcliffe, J. S. Ogden, and D. D. Oswald, *J.C.S. Chem. Comm.*, 1972, 338.

[7] H. Huber, P. Kundig, M. Moskovits, and G. A. Ozin, *Nature, Phys. Sci.*, 1972, **235**, 98.

[8] J. H. Darling and J. S. Ogden, *Inorg. Chem.*, 1972, **11**, 666.

[9] G. A. Ozin, personal communication.

[10] J. S. Anderson and J. S. Ogden, *J. Chem. Phys.*, 1969, **51**, 4189.

[11] See for example ' Vapor Pressure of the Chemical Elements,' eds. A. N. Nesmeyanov and R. Gary, Elsevier, New York, 1963.

cooled CsI window could be maintained at any fixed temperature between 15 and 33 K during sample deposition, and controlled diffusion studies were carried out up to *ca.* 40 K in argon, *ca.* 60 K in krypton, and up to *ca.* 80 K in xenon matrices. In order to minimise any effects due to variations in band shape with temperature however, i.r. spectra were recorded at a constant temperature of 20 K after such studies, and the full range of the Perkin-Elmer 225 spectrophotometer (5000—200 cm^{-1}) was made available through efficient dry air purging.

RESULTS

The initial experiments on this system were carried out using argon matrices, and it was shown[8] that the co-condensation of palladium atoms with 95% Ar–5% $C^{16}O$ mixtures at 27 K produced a strong band at 2070·3 cm^{-1} due to $Pd(C^{16}O)_4$. No other bands were observed which could be assigned to this molecule, and it was suggested that the three remaining i.r. active fundamentals were either too weak to be observed or that they all lie below 200 cm^{-1}. The first extensive studies on this system were therefore also carried out in argon, and attempted to locate these fundamentals by depositing for longer periods. These experiments showed that the co-condensation at 27 K of palladium atoms with argon containing 5% $C^{16}O$ regularly produced not only the strong band at 2070·3 cm^{-1} but also a much weaker feature at 261·7 cm^{-1} when deposition was carried out over a period of *ca.* 2 h. However, the spectrum obtained was found to be very dependent on the temperature of the central CsI window, and depositing at 15 K resulted in a more complicated spectrum in the terminal carbonyl region with additional bands appearing at 2056·5 and 2044·0 cm^{-1}. This suggested that considerable chemical reaction was taking place during quenching, and in an attempt to reduce its extent, the less volatile and more rigid matrix material krypton was employed. Using krypton, it was found that controlled diffusion studies could be carried out over a wider temperature range, and that spectra were sharper and better resolved. Bandwidths were now typically *ca.* 2 cm^{-1}, and there was less possibility of accidental overlap in $C^{18}O$ enrichment studies than in argon, where bandwidths were *ca.* 3 cm^{-1}. For these reasons the majority of experiments were subsequently carried out in krypton matrices, and the frequencies quoted in the text refer to krypton matrix experiments unless otherwise stated.

Figure 1a shows part of a typical i.r. spectrum obtained after co-condensing palladium atoms at 15 K with a large excess of krypton containing 5% $C^{16}O$. The very strong absorption centred near 2140 cm^{-1} is due to unreacted $C^{16}O$, and four prominent bands are also present at 2066·4, 2052·8, 2044·7, and 2040·1 cm^{-1} together with much weaker features at 2048·5, 2036·4, and 258·6 cm^{-1}. Traces of H_2O and CO_2 were also present in the matrix. Figure 1b shows the corresponding spectrum obtained after this sample was allowed to diffuse to *ca.* 55 K. A large number of similar experiments were carried out in which the proportion of CO in krypton was varied. Window temperatures were held constant at 15 K during deposition, and Table 1 compares the frequencies and relative band intensities observed in two of these with the corresponding results in argon.

This Table shows that there is a significant frequency shift between argon and krypton matrices, and that a much smaller shift is also observed for the same matrix gas doped with different amounts of CO. These small frequency shifts are quite typical and reflect slightly different molecular environments. However, it is evident from this data that varying either the matrix gas or the proportion of CO has a much more important effect on relative band intensities. Krypton matrices containing 0·2% CO give rise to a spectrum in which there is now typically only one prominent band at 2045·0 cm^{-1} together with several weaker features. After diffusion some of these weaker features remain unchanged, but bands at 2066·8, 2053·0, and 258·8 cm^{-1} increase in intensity, whilst the 2045·0 and 316·8 cm^{-1} bands decrease. The intensity changes observed in krypton–5% $C^{16}O$ deposits are illustrated in Figure 1.

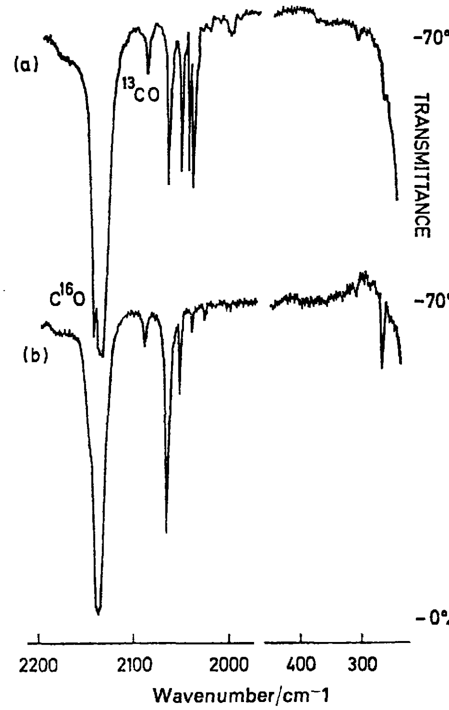

FIGURE 1 Infrared spectrum obtained after co-condensing Pd atoms with krypton–5% $C^{16}O$: (a), after deposition at 15 K; (b), the same sample after warming to *ca.* 55 K

On warming to *ca.* 35 K, the 2066·4 cm^{-1} band begins to increase in intensity, and after further diffusion to *ca.* 45 K this band is very prominent and the 2044·7 and 2040·1 cm^{-1} bands are significantly reduced. At *ca.* 55 K (Figure 1b), the 2044·7 cm^{-1} band has completely disappeared, and ultimately at *ca.* 60 K, only the 2066·4 and 2052·8 cm^{-1} bands remain in the terminal CO region. In the low frequency region, the weak feature at 258·6 cm^{-1} gains intensity throughout the diffusion.

It is not generally possible to carry out diffusion experiments in argon to temperatures higher than *ca.* 40 K, as argon has an appreciable vapour pressure[12] at this temperature, and begins to pump off, but, even at this relatively low temperature, significant changes were observed in argon–0·2% CO samples, and the 2070·8 cm^{-1} band increased in intensity. In xenon matrices, however, it is possible to study diffusion reactions up to *ca.* 80 K before the sample is

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[12] See for example, ' Scientific Foundations of Vacuum Technique,' eds. S. Dushman and J. M. Lafferty, Wiley, New York, 1962.

TABLE 1

Infrared vibration frequencies (cm^{-1}) and relative band intensities of matrix isolated palladium carbonyls

Krypton matrices				Argon matrices		
5% C^{16}O		0·2% C^{16}O				
Before diffusion	After diffusion	Before diffusion	After diffusion	5% C^{16}O	0·2% C^{16}O	Assignment
2066·4s	2066·4vs	2066·8vw	2066·8vs	2070·3vs	2070·8w	T_2 Pd(CO)$_4$
2052·8s	2052·8m		2053·0m	2056·5w	2057·5m	E' Pd(CO)$_3$
2044·7s		2045·0vs	2045·0m		2050·4w	PdCO
2040·1s	2040·1w	2040·4m	2040·4m	2044·0w	2044·2s	Σ_u^+ Pd(CO)$_2$
258·6w	258·6m		258·8m	261·7m		T_2 Pd(CO)$_4$
		316·8w				PdCO
Additional weaker features observed but not assigned						
2048·5w		2061·5vw	2061·5w		2060·5m	
2036·4w		2056·0m			2031·8w	
2003·5w	2003·5w	2025·3m	2025·3m		2008·7w	
		2016·8w	2016·8w			
			2003·8m			

Frequency accuracy ±0·3 cm^{-1}. All matrices were deposited at 15 K, and during the controlled diffusion samples were warmed to *ca.* 55 K. Relative band intensities refer to spectra recorded at 20 K.

lost, and although matrices were more highly scattering, a few experiments were carried out in an attempt to investigate whether any of these new species still persisted at liquid nitrogen temperatures. When palladium atoms were co-condensed with xenon–5% C^{16}O mixtures at 15 K, bands were observed at 2063·2, 2048·2, 2038·0, 2028·0, and 2024·0 cm^{-1}. On warming the matrix to 40 K, the band at 2063·2 cm^{-1} began to grow in intensity, and the other features began to decrease until eventually at *ca.* 65 K, only the 2063·2 cm^{-1} band remained. Warming to *ca.* 80 K produced no further change in the intensity of this band, but the broad feature due to unreacted C^{16}O began to decrease in intensity as CO was slowly pumped out of the matrix.

Several C^{18}O enrichment experiments were carried out in which both the C^{16}O : C^{18}O ratio and the proportion of total CO in the matrix were varied. The simplest spectrum was obtained when palladium atoms were co-condensed with krypton containing 0·1% C^{16}O + 0·1% C^{18}O, at 15 K. Only two strong bands were observed at 2045·0 and 2000·2 cm^{-1}, and these decreased on diffusion. Spectra became more complicated when the proportion of total CO was increased, and Figure 2a shows part of the i.r. spectrum obtained when palladium atoms were co-condensed with krypton containing 3·2% C^{16}O and 1·8% C^{18}O. Apart from the complexity of the 1970—2070 cm^{-1} region which is discussed below, one interesting feature is the appearance of two relatively weak bands at 2115·9 and 2107·6 cm^{-1} between the intense absorptions due to unreacted CO. These peaks were only observed in mixed C^{16}O–C^{18}O experiments, and appear to be associated with the four bands at 2066·4, 2033·4, 2025·2, and 2018·1 cm^{-1}, all of which increase in intensity on diffusion (Figure 2b). In this particular experiment, only a broad weak shoulder centred at 257·9 cm^{-1} was observed in the low frequency region. In an attempt to simplify this low frequency region, an experiment was therefore carried out with the maximum C^{18}O enrichment available (92%) under conditions where it is known [8] that only the tetracarbonyl is produced, *viz.*: co-condensing palladium atoms at 27 K with argon containing 5% total CO. In this experiment the terminal C–O stretching region showed an intense feature at 2022·0 cm^{-1} due [8] to Pd(C^{18}O)$_4$ and a weak feature at 2047·5 cm^{-1} due [8] to Pd(C^{16}O)(C^{18}O)$_3$, whilst in the low frequency region, a sharp, weak band was present at 258·0 cm^{-1}.

The frequencies observed in these C^{16}O–C^{18}O experiments are all listed in Tables 2—4.

DISCUSSION

As a result of varying the matrix gas and the proportion of carbon monoxide, and monitoring the changes in

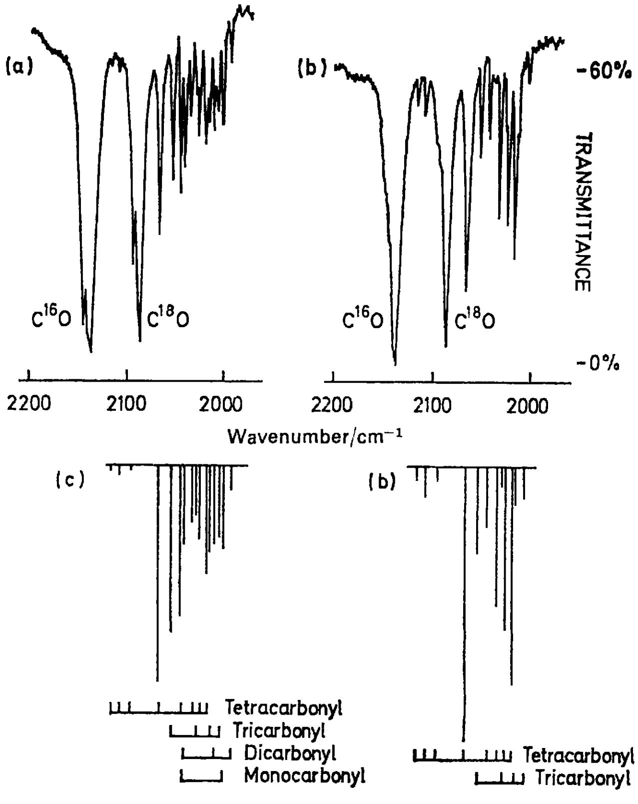

FIGURE 2 Observed and calculated infrared spectra obtained after co-condensing Pd atoms with krypton–3·2% C^{16}O + 1·8% C^{18}O: (a), after deposition at 15 K; (b), after diffusion to *ca.* 55 K; (c), calculated spectrum before diffusion; (d), calculated spectrum after diffusion

TABLE 2

Vibration frequencies (cm^{-1}) of matrix isolated palladium tetracarbonyls

Argon	Krypton		
Observed [a]	Observed [b]	Calc. [c]	Assignment
2070·3	2066·4	2067·3	T_2 $Pd(C^{16}O)_4$
		2067·3	E $Pd(C^{16}O)_3(C^{18}O)$
		2067·3	B_1 $Pd(C^{16}O)_2(C^{18}O)_2$
2047·5	2044·0	2043·5	A_1 $Pd(C^{16}O)(C^{18}O)_3$
2037·0	2033·4	2032·7	A_1 $Pd(C^{16}O)_2(C^{18}O)_2$
2029·0	2025·2	2024·4	A_1 $Pd(C^{16}O)_3(C^{18}O)$
2022·0	2018·1	2017·5	T_2 $Pd(C^{18}O)_4$
		2017·5	E $Pd(C^{16}O)(C^{18}O)_3$
		2017·5	B_2 $Pd(C^{16}O)_2(C^{18}O)_2$
(Inactive)	(Inactive)	2124·1	A_1 $Pd(C^{16}O)_4$
	2115·9	2116·8	A_1 $Pd(C^{16}O)_3(C^{18}O)$
	2107·6	2108·2	A_1 $Pd(C^{16}O)_2(C^{18}O)_2$
		2097·0	A_1 $Pd(C^{16}O)(C^{18}O)_3$
(Inactive)	(Inactive)	2072·9	T_2 $Pd(C^{18}O)_4$
261·7	258·6		T_2 $Pd(C^{16}O)_4$
258·0			T_2 $Pd(C^{18}O)_4$

[a] Ref. 8. [b] Frequency accuracy $\pm 0{\cdot}3$ cm^{-1}. [c] Assuming $K_{CO} = 17{\cdot}50$ and $K_{CO,CO} = 0{\cdot}24$ mdyr Å^{-1}.

TABLE 3

Carbonyl vibration frequencies (cm^{-1}) of isotropically substituted palladium tricarbonyls in krypton matrices

Observed [a]	Calc. [b]	Assignment
2052·8	2053·7	E' $Pd(C^{16}O)_3$
	2053·7	B_2 $Pd(C^{16}O)_2(C^{18}O)$
2027·3	2027·7	A_1 $Pd(C^{16}O)(C^{18}O)_2$
2014·9	2014·4	A_1 $Pd(C^{16}O)_2(C^{18}O)$
2005·2	2004·2	E' $Pd(C^{18}O)_3$
	2004·2	B_2 $Pd(C^{16}O)(C^{18}O)_2$
(Inactive)	2120·6	A_1' $Pd(C^{16}O)_3$
	2109·9	A_1 $Pd(C^{16}O)_2(C^{18}O)$
	2096·1	A_1 $Pd(C^{16}O)(C^{18}O)_2$
(Inactive)	2069·5	A_1' $Pd(C^{18}O)_3$

[a] Frequency accuracy $\pm 0{\cdot}3$ cm^{-1}. [b] Assuming $K_{CO} = 17{\cdot}41$ and $K_{CO,CO} = 0{\cdot}375$ mdyn Å^{-1}.

TABLE 4

Carbonyl vibration frequencies (cm^{-1}) of isotopically substituted palladium dicarbonyls in krypton matrices

Observed [a]	Calc. [b]	Assignment
2040·1	2040·7	Σ_u^+ $Pd(C^{16}O)_2$
2009·4	2009·4	Σ^+ $Pd(C^{16}O)(C^{18}O)$
1992·0	1991·5	Σ_u^+ $Pd(C^{18}O)_2$
(Inactive)	2130·0	Σ_g^+ $Pd(C^{16}O)_2$
	2111·0	Σ^+ $Pd(C^{16}O)(C^{18}O)$
(Inactive)	2078·7	Σ_g^+ $Pd(C^{18}O)_2$

[a] Frequency accuracy $\pm 0{\cdot}3$ cm^{-1}. [b] Assuming $K_{CO} = 17{\cdot}57$ and $K_{CO,CO} = 0{\cdot}75$ mdyn Å^{-1}.

relative band intensities which take place on diffusion, it is clear that at least thirteen distinct bands may be assigned to palladium carbonyls, and that the four most prominent bands at 2066·4, 2052·8, 2044·7, and 2040·1 cm^{-1} (Figure 1) are each associated with a different chemical species. By analogy with DeKock's matrix synthesis of nickel carbonyls,[2] it is possible to interpret the diffusion behaviour of these four bands in terms of the stepwise addition of matrix trapped CO to PdCO, $Pd(CO)_2$, and $Pd(CO)_3$ and to assign them to the species $Pd(CO)_4$, $Pd(CO)_3$, PdCO, and $Pd(CO)_2$ respectively. The remaining terminal CO bands might then be assigned to polynuclear species.

It has been shown, however, that the use of $C^{18}O$ enrichment in the matrix synthesis of metal carbonyls allows one to identify the stoicheiometry and symmetry of certain simple binary carbonyls by characteristic frequency and intensity patterns,[1] and that in particular, the species $M(CO)_4$ T_d, $M(CO)_3$ D_{3h}, $M(CO)_2$ $D_{\infty h}$, and MCO would give rise to prominent quintet, quartet, triplet, and doublet patterns respectively under these conditions. Fourteen prominent bands should thus be observed in the $C^{16}O$–$C^{18}O$ matrix synthesis of a mixture of these molecules.

In these experiments, it was only possible to carry out $C^{18}O$ enrichment studies on the four most prominent palladium carbonyl bands, and the effect of this is shown in Figure 2. Thirteen distinct bands are observed in the frequency range 1970—2070 cm^{-1} at 2066·4, 2052·8, 2044·7, 2040·1, 2033·4, 2027·3, 2025·2, 2018·1, 2014·9, 2009·4, 2005·2, 1999·9, and 1992·0 cm^{-1}, and the detailed assignments of these and other weaker features are discussed below. Several papers [13] have described how one may set up the F and G matrices for metal carbonyl vibrations using Cotton–Kraihanzel force constants in the ' high frequency separation ' approximation, and this aspect will not be discussed here in detail.

$Pd(CO)_4$.—The previous reports describing the characterisation of this molecule in low temperature matrices are in close agreement. Ozin *et al.*[7] observed a prominent i.r. band at 2066·3 cm^{-1} with a shoulder at 2071·8 cm^{-1} when palladium atoms were co-condensed in a large excess of pure $C^{16}O$, whilst the Raman spectra [9] of similar deposits showed two bands at 2122 and 2066 cm^{-1}, which were assigned as the A_1 and T_2 carbonyl vibrations of $Pd(C^{16}O)_4$. When the same authors deposited palladium atoms in an argon matrix containing 1% CO at *ca.* 12 K, a more complicated i.r. spectrum was obtained, but it was suggested on the basis of diffusion studies that a band now observed at 2070·9 cm^{-1} could be assigned to the tetracarbonyl. Darling and Ogden [8] observed a single i.r. band at 2070·3 cm^{-1} when palladium atoms were co-condensed at 27 K with argon containing 5% CO, and by using $C^{18}O$ enrichment were able to show that this was the T_2 carbonyl stretching vibration of tetrahedral $Pd(C^{16}O)_4$. No other vibrations of this molecule have been reported.

The results obtained here in krypton matrices in the first place confirm that $Pd(CO)_4$ is the stable diffusion product in this system. Figure 1 shows that in the terminal CO stretching region, a strong band at 2066·4 cm^{-1} grows on diffusion at the expense of three other bands. Figures 2a and 2b show the effect of 36% ^{18}O enrichment on the same system, where six bands at 2066·4, 2033·4, 2025·2, 2018·1, 2115·9, and 2107·6 cm^{-1} are now found to increase in intensity on diffusion. It has been shown [1] that the maximum number of distinct i.r. bands expected in the matrix synthesis of isotopically mixed palladium tetracarbonyls $Pd(C^{16}O)_n(C^{18}O)_{4-n}$

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[13] (*a*) L. M. Haines and M. H. B. Stiddard, *Adv. Inorg. Chem., Radiochem.*, 1969, **12**, 53; (*b*) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432; (*c*) H. Haas and R. K. Sheline, *J. Chem. Phys.*, 1967, **47**, 2996; (*d*) G. Bor, *J. Organometallic Chem.*, 1967, **10**, 343.

(n = 0—4) is eight, and the six bands listed above are all due to these species. A detailed band assignment is given in Table 2, and both the relative intensities and the positions of these bands, calculated using the procedures described earlier,[1] are shown in Figures 2c and 2d. These calculations show that in addition to the six bands listed above, two further bands are predicted at 2043·5 and 2097·0 cm^{-1}. Although the latter is expected to be relatively weak, and is almost certainly overlapped by the broad absorption of unreacted $C^{18}O$ (Figure 2), a moderately intense component of the characteristic quintet should be present at *ca.* 2043·5 cm^{-1} in Figure 2a, and should increase in intensity on diffusion. Figure 2b shows that a band does in fact remain after diffusion at 2044·0 cm^{-1}, but appears to have *decreased* in intensity compared with Figure 2a. The reason for this anomaly lies in accidental band overlap. Figure 1 shows that in addition to the 2066·4 cm^{-1} band, which grows on diffusion, a strong band is also present at 2044·7 cm^{-1} which completely disappears on warming to 55 K. In the corresponding $C^{16}O$–$C^{18}O$ experiment, this band initially contributes strongly to the prominent absorption at 2044·7 cm^{-1} in Figure 2a, but decreases on diffusion to reveal the underlying tetracarbonyl band. Seven of the eight bands expected are thus observed, and using the two independent force constants $K_{CO} = 17·50$ mdyn $Å^{-1}$ and $K_{CO,CO} = 0·24$ mdyn $Å^{-1}$ the calculated and observed frequencies agree to within 1 cm^{-1} (Table 2), thus confirming the assignment.

The frequencies reported here in krypton are uniformly *ca.* 4 cm^{-1} lower than the corresponding bands observed previously[8] in argon, and it is significant that in xenon matrices this diffusion product shows a further shift to low frequency of 3·2 cm^{-1}. No attempt is made here to account for the magnitude of these shifts, but as a result of such perturbations the Cotton–Kraihanzel force constants obtained will be dependent on the matrix used.

The most significant feature of the krypton matrix diffusion, however, is the growth of a relatively weak low frequency band at 258·6 cm^{-1} (Figure 1). This band was always found to be *ca.* 8% as intense as the 2066·4 cm^{-1} absorption over a wide range of experimental conditions, and is therefore assigned to a second i.r. active fundamental of $Pd(C^{16}O)_4$. The additional experiments carried out in argon matrices provide further confirmation of this assignment. Although previous experiments[8] had failed to locate any low frequency bands, prolonged deposition under conditions where only $Pd(C^{16}O)_4$ is formed resulted in an intense carbonyl band at 2070·3 cm^{-1} and a weaker band at 261·7 cm^{-1}, which shifted to 258·0 cm^{-1} on 92% ^{18}O enrichment. This band was thus clearly distinguished from any residual water vapour absorptions present in this region of the spectrum.

Molecular $Pd(C^{16}O)_4$ has a total of four i.r. active vibrations. These all have T_2 symmetry, and may be thought of as a C–O stretching mode, a Pd–C stretching mode, a Pd–C–O bending mode, and a C–Pd–C bending mode. The first of these has already been assigned and discussed, and by analogy[14] with $Ni(C^{16}O)_4$, in which the C–Ni–C band lies at 80 cm^{-1}, it is very unlikely that we would observe the C–Pd–C bend in the range of our spectrometer (5000—200 cm^{-1}). The low frequency band observed here must therefore be either the Pd–C stretch or the Pd–C–O bend. In $Ni(C^{16}O)_4$, the corresponding Ni–C and Ni–C–O vibrations lie at 423·1 and 458·9 cm^{-1} in the gas phase,[14] and the former is considerably more intense. When DeKock synthesised $Ni(CO)_4$ from Ni atoms and CO in an argon matrix,[2] he observed a low frequency tetracarbonyl band at 435 cm^{-1} and assigned this as the Ni–C stretch. It thus seems reasonable to assign the 258·6 cm^{-1} band observed here in krypton matrices to the T_2 Pd–C stretching mode rather than the Pd–C–O bend.

One curious feature concerning the T_2 vibrations of $Ni(CO)_4$ is that although the 423·1 and 458·9 cm^{-1} bands are close together, the potential energy distribution[14] indicates that they may be quite accurately described as Ni–C stretching and Ni–C–O bending modes, and that contrary to expectation,[13a] there appears to be very little coupling between them. One consequence of this is that quite a good estimate of the Ni–C stretching force constant may be obtained directly from the 423·1 cm^{-1} band without carrying out a full normal coordinate analysis. Thus whereas an extended analysis[14] based upon a large number of vibration frequencies yields a T_2 symmetry force constant $F_{NiC} = 1·98$ mdyn $Å^{-1}$, a very much simpler analysis which treats $Ni(C^{16}O)_4$ as an XY_4 molecule[15] with masses X = 58·7 (Ni) and Y = 28 ($C^{16}O$) gives $F_{NiC} = 1·80$ mdyn $Å^{-1}$. This value is obtained using only the single Ni–C stretching frequency at 423·1 cm^{-1}, and lies just outside the error limits (+0·13, −0·14) quoted for the more extensive analysis.

There is clearly insufficient data on $Pd(CO)_4$ to carry out a vibrational analysis comparable with that obtained[14] for $Ni(CO)_4$, but if one assumes that in $Pd(CO)_4$, the Pd–C and Pd–C–O vibrations are similarly uncoupled, it is possible to obtain an estimate for the PdC stretching force constant using the above simplification. The value obtained from the krypton matrix absorption at 258·6 cm^{-1} is 0·82 mdyn $Å^{-1}$, and even if this parameter were in error by as much as 50%, there would still be a significant difference between the Ni–C and Pd–C force constants.

Substitution by $C^{18}O$ lowers the frequency of the metal–carbon vibration in both molecules. In $Ni(C^{18}O)_4$, the Ni–C stretching mode occurs at 416·6 cm^{-1} in the gas phase, and this may be compared with a value of 414·1 cm^{-1} calculated from the extended analysis.[14] The simple force field (Y = 30) predicts that the Pd–C stretching mode for $Pd(C^{18}O)_4$ trapped in argon should

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[14] L. H. Jones, R. S. McDowell, and M. Goldblatt, *J. Chem. Phys.*, 1968, **48**, 2663.

[15] See for example G. Herzberg, 'Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules,' Van Nostrand, Princeton, N.J., 1945.

occur at 255·2 cm^{-1}, and this may be compared with the observed band at 258·0 cm^{-1}.

The low value of the Pd–C stretching constant suggests that the Pd–C bond is rather weak, and may partially explain why $Pd(CO)_4$ has not yet been prepared by standard synthetic methods. However, diffusion experiments in xenon matrices indicate that $Pd(CO)_4$ is thermally stable up to *ca.* 80 K and it may therefore be possible to prepare this compound on the gram scale using the metal atom co-condensation techniques described by Timms.[16]

$Pd(CO)_3$.—The band at 2052·8 cm^{-1} disappears only slowly on diffusion (Figure 1) and is assigned to $Pd(C^{16}O)_3$. Enrichment with $C^{18}O$ produces a quartet pattern at 2052·8, 2027·3, 2014·9, and 2005·2 cm^{-1} characteristic[1] of this stoicheiometry, and the absence of any other i.r. active carbonyl band which could be assigned to this species suggests that the molecule is planar with D_{3h} symmetry. A detailed band assignment is given in Table 3 together with the corresponding frequencies calculated using the principal and interaction carbonyl force constants $K_{CO} = 17{\cdot}41$ and $K_{CO,CO} = 0{\cdot}375$ mdyn Å^{-1}. The line spectra calculated before and after diffusion are shown in Figures 2c and 2d. The high frequency A_1 components of $Pd(C^{16}O)_2C^{18}O$ and $Pd(C^{16}O)(C^{18}O)_2$ expected at 2109·9 and 2096·1 cm^{-1} were not observed in these experiments. Not only do these bands lie in a region of the spectrum masked by unreacted CO, but their intensity is calculated to be very low, and they cannot be adequately represented on the line spectra. $Pd(CO)_3$ has not previously been characterised, but Ozin *et al.*[9] report the existence of a band at 2060 cm^{-1} in argon matrices which is assigned to this species on the basis of diffusion studies. Our experiments in argon (Table 1) place this band at *ca.* 2057 cm^{-1}. In the corresponding Ni–CO system, DeKock[2] assigns a carbonyl band at 2017 cm^{-1} to the planar D_{3h} species $Ni(CO)_3$.

The results obtained here show that the principal force constant K_{CO} is smaller in $Pd(CO)_3$ than in $Pd(CO)_4$, and that the interaction constant $K_{CO,CO}$ is larger. It is possible to interpret these differences in terms of changes in the Pd–C–O electron distribution in the two molecules, but we do not believe that the observed frequencies are a sufficient indication of this. Not only are they uncorrected for anharmonicity, but they also show a significant dependence on the matrix.

PdCO.—A relatively simple spectrum was obtained when palladium atoms were co-condensed with krypton containing 0·2% $C^{16}O$ and only one strong band (Table 1) was observed. When this experiment was repeated using $C^{18}O$ enrichment, this absorption appeared as a strong doublet at 2045·0 and 2000·2 cm^{-1}, and the parent species is therefore identified as a monocarbonyl. In a krypton–5% CO matrix, the $PdC^{16}O$ band appears at 2044·7 cm^{-1}, and rapidly decreases on diffusion (Figure 1). The accidental overlap of this band with an isotopically substituted tetracarbonyl absorption in $C^{18}O$ enrichment experiments, has already been discussed, but it is relevant to note that no such overlap complicates the $PdC^{18}O$ band at 1999·9 cm^{-1} (Figure 2a) which completely disappears on diffusion.

For this particular molecule, there is only one carbonyl force constant, K_{CO}, and the best fit with the observed frequencies is obtained by putting $K_{CO} = 16{\cdot}92$ mdyn Å^{-1}. This parameter reproduces the $PdC^{16}O$ and $PdC^{18}O$ bands at 2047·1 and 1997·8 cm^{-1} respectively, but both these frequencies differ from the observed bands by *ca.* 2 cm^{-1}. The error here is at least twice that found for the other palladium carbonyls, and indicates that the high frequency separation is no longer quite so satisfactory.

It has been tacitly assumed so far that there is only one atom of palladium in this monocarbonyl, but it is clear that using the high frequency separation approximation, the existence of only one CO group can convey no information about the symmetry of the species or about the number of metal atoms present. However, the fact that palladium vapour is largely monatomic,[11] and that a molecule such as $Pd(CO)_4$ is ultimately produced on diffusion, strongly suggests that PdCO is the species initially formed, rather than, for example Pd_2CO. In the corresponding nickel atom experiments, DeKock[2] observed an analogous species NiCO which reacted with CO during diffusion to produce $Ni(CO)_4$, and this behaviour would seem to have a close parallel here.

In the low frequency region, one weak band was observed at 316·8 cm^{-1} which rapidly disappeared on diffusion, and is tentatively assigned as a second fundamental vibration of this species. It was not possible to carry out isotope studies on this band in these experiments, but in principle, this additional information would not only confirm the existence of one Pd–C bond, but would also allow one to distinguish between linear and bent structures.

$Pd(CO)_2$.—The fourth prominent band in Figure 1 lies at 2040·1 cm^{-1}. This band also decreases significantly in diffusion, but $C^{18}O$ enrichment yields a triplet structure at 2040·1, 2009·4, and 1992·0 cm^{-1} in which the central band is relatively intense. No other absorptions showed this behaviour, and the triplet pattern is therefore characteristic[1] of a *linear* dicarbonyl with $D_{\infty h}$ symmetry. On the basis of earlier arguments, it is assumed that only one palladium atom is present, and the assignment of the observed frequencies to isotopically labelled $Pd(CO)_2$ molecules is given in Table 4. There is good agreement between the observed and calculated bands if one puts $K_{CO} = 17{\cdot}57$ and $K_{CO,CO} = 0{\cdot}75$ mdyn Å^{-1} but there is now no independent check on these force constants as the high frequency Σ^+ mode of $Pd(C^{16}O)(C^{18}O)$ is too weak to be observed. However, indirect confirmation that these parameters are reasonable is provided by the calculated intensity pattern, which is a function[1] of these force constants. The line spectrum in Figure 2c shows that the calculated pattern for $Pd(CO)_2$ species is in good agreement with the observed spectrum in Figure 2a.

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[16] P. L. Timms, *J. Chem. Soc.* (*A*), 1970, 2526.

Other Features.—Table 1 shows that several weak carbonyl bands were observed in both krypton and argon matrices in addition to the more prominent bands assigned above. None of these grew on diffusion, and they are tentatively assigned to species containing more than one atom of palladium rather than higher carbonyls such as $Pd(CO)_5$ or $Pd(CO)_6$. Throughout these studies, no bands were observed in the bridging carbonyl region, and this suggests that these additional bands are terminal carbonyl vibrations of species $Pd_x(CO)_y$ where Pd_x represents a small cluster of palladium atoms. This interpretation is similar to that suggested by Burdett *et al.*[17] in their characterisation of metal dinitrogen complexes, and it is significant that these bands are generally produced in matrices containing small amounts of CO where the reaction $Pd + PdCO \longrightarrow Pd_2CO$ is a realistic alternative to $CO + PdCO \longrightarrow Pd(CO)_2$.

Diffusion Reactions.—Controlled diffusion studies have been employed in this work primarily as a method of distinguishing between the different chemical species produced. However, from the above band assignments, it is evident that the significant intensity changes observed during diffusion (Table 1) are the result of the addition of carbon monoxide to lower carbonyl species to yield ultimately $Pd(CO)_4$. In this respect, these Pd atom–CO experiments are very similar to DeKock's Ni atom–CO system.[2]

In principle, these intensity changes might be used to study the detailed kinetics of addition reactions such as (1), but in practice the situation is complicated by two

$$Pd(CO)_n + CO \longrightarrow Pd(CO)_{n+1} \qquad (1)$$

factors. It is not possible, using i.r. spectroscopy, to determine the concentration of free palladium atoms trapped in the matrix, and there is some uncertainty concerning the nature of matrix-isolated carbon monoxide. Leroi *et al.*[18] have shown that at very low concentrations (*ca.* 1 : 8000) carbon monoxide is isolated as a simple monomer in argon, and has a single sharp absorption at 2148·8 cm^{-1}. In more concentrated matrices however, this band is accompanied by a broad polymer feature at 2138 cm^{-1}. These studies have been extended by Davies and Hallam[19] who conclude that CO aggregates are present in a number of different matrices.

The proportion of CO employed in these experiments was varied from 0·1 to 10%, and before diffusion, spectra typically showed both a sharp high frequency monomer band and a broader polymer absorption (*e.g.* Figure 1). Any of these species might react to produce higher palladium carbonyls, and although it is possible that only the monomer is involved (equation 1), reactions involving polymeric CO

$$Pd(CO)_n + (CO)_m \longrightarrow Pd(CO)_{n+1} + (CO)_{m-1}$$

cannot be discounted. Despite these difficulties in interpreting the detailed diffusion kinetics, it is evident that all these reactions must involve very low activation energies, and it is not therefore surprising that they also appear to take place, to a limited extent, during deposition. Table 1 shows that matrices containing 5% CO yield relatively more of the higher carbonyls $Pd(CO)_3$ and $Pd(CO)_4$ than those containing only 0·1% CO, and this effect cannot be purely statistical, since argon matrices always yield relatively more of the higher carbonyls than krypton matrices with the same CO concentration. The extent of these diffusion reactions can also be increased by depositing at window temperatures above 15 K when quenching is less rapid, and this would appear to be the main reason why only $Pd(CO)_4$ is observed in argon–5% CO matrices deposited at 27 K.

CONCLUSIONS

The results described here show that several binary palladium carbonyls are produced when palladium atoms are co-condensed at low temperatures with matrices containing a few mole % CO. With the aid of $C^{18}O$ enrichment, the four most prominent species are shown to be $Pd(CO)_4$ T_d, $Pd(CO)_3$ D_{3h}, $Pd(CO)_2$ $D_{\infty h}$, and PdCO, and diffusion experiments indicate that the tetracarbonyl is stable up to *ca.* 80 K. Vibration frequencies were slightly matrix-dependent, but the agreement between the observed and calculated i.r. spectra in the terminal CO region was found to be satisfactory, and the corresponding Cotton–Kraihanzel force constants have been obtained. In the low frequency region, a band assigned to the T_2 Pd–C stretching vibration in $Pd(CO)_4$ yields an estimated Pd–C stretching constant of 0·82 mdyn $Å^{-1}$ which is considerably lower than the metal–carbon stretching constant in $Ni(CO)_4$.

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[2/2643 *Received, 22nd November,* 1972]

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[19] J. B. Davies and H. E. Hallam, *J.C.S. Faraday II*, 1972, **68**, 509.