$(CH_3)_2PB_5H_8$:[4] with $(CH_3O)_3B$ as the reference, there was a doublet at 18.9 ppm (J = 158 cps), an equally intense pseudotriplet at 41.5 ppm ("J" = 113 cps), and a doublet half as intense at 63.4 ppm (J = 153 cps). These features would correspond, respectively, to the 4,5-B, the 2,3-P-bridged B, and the 5-B atoms. Possible isomers, like those of $CH_3CF_3PB_5H_8$,[4] were not observed.

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Infrared Spectroscopic Evidence for Palladium Tetracarbonyl

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Binary carbonyls are known for a wide range of transition metals,[1] but although nickel tetracarbonyl was one of the first to be characterized, there appears to be very little evidence for the corresponding palladium carbonyl $Pd(CO)_4$. This is presumably because attempts to prepare this compound by routine methods have failed. Quite recently, however, Timms[2] has demonstrated that zerovalent organometallic compounds can readily be prepared by a new synthetic route in which metal atoms are cocondensed at low temperatures with a suitable ligand. If cocondensation takes place at 4°K in the presence of an inert gas, then this method closely resembles a typical matrix-isolation experiment, and, in particular, DeKock[3] has shown that when nickel atoms are cocondensed with Ar–CO mixtures in this way, nickel carbonyls are obtained.

We have been studying the parallel reaction between palladium atoms and Ar–CO mixtures deposited at cryogenic temperatures, and this note describes the characterization of palladium tetracarbonyl.

Experimental Section

A detailed description of the apparatus used for this work is described elsewhere.[4] In these experiments, palladium atoms were produced by heating palladium wire (99.99% pure) to ~1800°K and were cocondensed with a large excess (~1000-fold) of Ar–CO mixture on a cesium iodide window cooled to ~20°K. High-purity (Grade "X") argon and carbon monoxide ($C^{16}O$) were supplied by the British Oxygen Co., while samples of 90 atom % ^{18}O-enriched carbon monoxide were obtained from Miles Laboratories, Inc.

In a series of preliminary experiments, the mixtures of argon and carbon monoxide were varied in composition from 99% Ar–1% CO to 90% Ar–10% CO, and the window temperature was also varied. These experiments established that a number of different palladium carbonyl species could be formed depending mainly upon the Ar:CO ratio and to a lesser extent upon the temperature of the cesium iodide window. Thus the spectrum obtained from cocondensing Pd atoms with 99% Ar–1% CO at 15°K was quite different from that obtained using 90% Ar–10% CO at 27°K. Deposition rates were held constant at ~5 mmol/hr.

A detailed discussion of all the possible palladium carbonyls produced under different experimental conditions is beyond the scope of this note and will be presented in a future paper. However, a very simple spectrum was always obtained using a 95% Ar–5% CO mixture deposited at 27°K, and the results described here refer specifically to these conditions.

Results

Figure 1a shows part of the infrared spectrum obtained when palladium atoms are cocondensed at 27°K with a large excess of Ar–$C^{16}O$ (95% Ar–5% CO). A single palladium carbonyl peak is observed at 2070.3 cm^{-1}, and no other absorptions were noted apart from a strong band due to unreacted carbon monoxide and traces of CO_2 and H_2O. When we condensed nickel atoms under these conditions in a separate experiment, a prominent band was observed at 2050 cm^{-1} which is assigned by DeKock[3] to $Ni(CO)_4$. This suggests that the single peak in the Pd–Ar–CO experiment arises from the corresponding palladium tetracarbonyl, and this assignment is confirmed in experiments using Ar–$C^{16}O$–$C^{18}O$ mixtures.

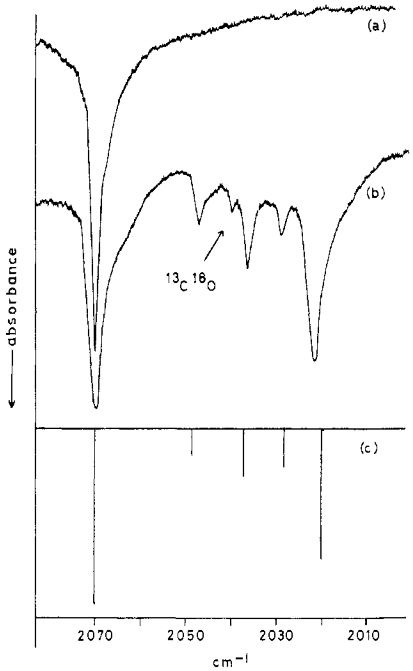

Figure 1.—(a) Infrared spectrum obtained from cocondensation of Pd atoms with Ar–$C^{16}O$ at 27°K. (b) Infrared spectrum obtained from cocondensation of Pd atoms with Ar–$C^{16}O$–$C^{18}O$ at 27°K. (c) Calculated spectrum for $Pd(C^{16}O)_n(C^{18}O)_{4-n}$ species.

Figure 1b shows the corresponding spectrum obtained when palladium atoms are condensed with a mixture of 95% Ar–2.7% $C^{16}O$–2.3% $C^{18}O$. This spectrum shows five prominent bands at 2070.3, 2047.5, 2037.0, 2029.0, and 2022.0 cm^{-1} due to Pd–$C^{16}O$–$C^{18}O$ species together with a weak feature at 2039.8 cm^{-1} which is due to matrix-isolated $^{13}C^{18}O$.

Discussion

If one assumes that the terminal C–O stretching vibrations in metal carbonyls may be "factored off" from the remaining vibrations of the molecule, it is then fairly straightforward[5] to calculate both the vibration frequencies and relative infrared band intensities for all

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[1] E. W. Abel and F. G. A. Stone, *Quart. Rev., Chem. Soc.*, **24**, 498 (1970).

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

[3] R. L. DeKock, *Inorg. Chem.*, **10**, 1205 (1971).

[4] J. S. Anderson and J. S. Ogden, *J. Chem. Phys.*, **51**, 4189 (1969).

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the possible mixed ($C^{16}O$–$C^{18}O$) carbonyls. In particular, this has been done for the molecular species $Ni(^{12}C^{16}O)_n(^{13}C^{16}O)_{4-n}$ by Bor[6] and by Haas and Sheline.[7] For a $^{12}CO:^{13}CO$ ratio close to unity and complete CO isotope scrambling, these calculations predict that in the C–O stretching region there will be five relatively intense bands which correlate with the F_2 mode in the isotopically pure (n = 0 or 4) carbonyl. As a result of band overlap, the two outer peaks of this quintet are expected to be significantly more intense than the three central bands. Three much weaker bands which correlate with the inactive A_1 mode in the pure carbonyl are also predicted at higher frequencies. The positions of all the C–O stretching vibrations may be calculated using only two independent parameters. These are the Cotton–Kraihanzel force constants,[8] which in Haas and Sheline's paper[7] are identified as K_s, the principal C–O stretching constant, and K_c, the CO–CO interaction constant. Calculation of the relative band intensities requires, in addition, knowledge of the $^{12}CO:^{13}CO$ isotope ratio in order that the relative abundances of the five possible carbonyls (n = 0–4) may be obtained.

We have carried out a parallel analysis assuming that the Pd–$C^{16}O$–$C^{18}O$ bands observed in this work arise from palladium tetracarbonyl. The use of ^{18}O rather than ^{13}C makes no qualitative difference to the spectrum, and one again expects a well-defined quintet. Table I compares the frequencies calculated for the species $Pd(C^{16}O)_n(C^{18}O)_{4-n}$ with the bands observed in Figure 1b, while Figure 1c shows the expected intensity pattern calculated from the known $C^{16}O:C^{18}O$ ratio of 1.17.

There is good agreement between the calculated and observed frequencies which suggests that the bands have been correctly assigned, and the Cotton–Kraihanzel force constants derived from the analysis are reasonable. The principal C–O stretching constant K_s has the value 17.55 mdyn/Å while the interaction constant K_c is 0.295 mdyn/Å. These may be compared with the values 17.246 and 0.336 mdyn/Å which have been obtained for $Ni(CO)_4$ using this approach.[6] The calculated band intensities provide additional confirmation for $Pd(CO)_4$ in that the quintet pattern is characteristic of a tetracarbonyl with T_d symmetry. We were unfortunately not able to observe the three A_1 modes predicted above 2100 cm^{-1} (see Table I). Not only are they expected to be much less intense than the observed quintet, but they would also be partly overlapped by the bands due to unreacted carbon monoxide.

TABLE I

CARBONYL VIBRATION FREQUENCIES (CM^{-1}) OF PALLADIUM TETRACARBONYLS

Calcd[a]	Obsd[b]	Assignment
2070.3	2070.3	F_2 $Pd(C^{16}O)_4$
2070.3		E $Pd(C^{16}O)_3(C^{18}O)$
2070.3		B_1 $Pd(C^{16}O)_2(C^{18}O)_2$
2048.6	2047.5	A_1 $Pd(C^{16}O)(C^{18}O)_3$
2037.0	2037.0	A_1 $Pd(C^{16}O)_2(C^{18}O)_2$
2028.0	2029.0	A_1 $Pd(C^{16}O)_3(C^{18}O)$
2020.4	2022.0	F_2 $Pd(C^{18}O)_4$
2020.4		E $Pd(C^{16}O)(C^{18}O)_3$
2020.4		B_2 $Pd(C^{16}O)_2(C^{18}O)_2$
2139.8	Inactive	A_1 $Pd(C^{16}O)_4$
2131.8	...	A_1 $Pd(C^{16}O)_3(C^{18}O)$
2122.4	...	A_1 $Pd(C^{16}O)_2(C^{18}O)_2$
2110.3	...	A_1 $Pd(C^{16}O)(C^{18}O)_3$
2088.2	Inactive	A_1 $Pd(C^{18}O)_4$

[a] Assuming K_s = 17.55 mdyn/Å and K_c = 0.295 mdyn/Å. [b] Frequency accuracy ±0.5 cm^{-1}.

In the low-frequency region, the spectrum of nickel tetracarbonyl[9] shows a further three infrared-active fundamentals at 459 cm^{-1} (Ni–C–O bend), 423 cm^{-1} (Ni–C stretch), and 80 cm^{-1} (C–Ni–C bend). Our spectrometer[4] has a frequency range of 5000–200 cm^{-1}, and although the C–Pd–C bending mode in $Pd(CO)_4$ almost certainly lies below this range, we had expected to see the corresponding Pd–C stretch and the Pd–C–O bend. No such bands have yet been observed, and we conclude that these vibrations either have very low extinction coefficients or, alternatively, that they also lie below 200 cm^{-1}. The latter explanation implies that the Pd–C bond is relatively weak and, if this is true, may partly explain why palladium carbonyls have not been prepared directly from palladium metal and CO.

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