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Infrared Spectral Evidence for the Formation of the New Complexes Dicarbonyldinitrosylosmium and Tetracarbonylcobalt in Frozen Gas Matrices at 20 K

By **Oliver Crichton, Martyn Poliakoff, Antony J. Rest,*** and **James J. Turner,***† University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

I.r. spectroscopy provides evidence for the photochemical reaction of pentacarbonylosmium with nitrogen oxide in argon matrices at 20 K to produce the hitherto unknown complex dicarbonyldinitrosylosmium $[Os(CO)_2(NO)_2]$. In the reverse of this type of reaction, photolysis of dicarbonyldinitrosyliron, tricarbonylnitrosylcobalt, and tetracarbonylnitrosylmanganese in pure carbon monoxide matrices produces mononuclear carbonyl species. Isotopic substitution suggests that the cobalt species is tetracarbonylcobalt $[Co(CO)_4]$ with C_{3v} geometry.

PHOTOLYSIS of stable molecules isolated in a frozen matrix of an inert gas has been widely used as a method of generating unstable fragments for spectroscopic investigation.[1] Pentacarbonyl complexes of chromium, molybdenum, and tungsten have been obtained by u.v. photolysis of the parent hexacarbonyl complexes in hydrocarbon glasses[2] and argon matrices.[3] Photochemically produced fragments can be used to synthesise new compounds by reaction either with a substrate added to the matrix, *e.g.* HO_2 by the photolysis of HI in an argon matrix containing oxygen,[4] or with the matrix itself, *e.g.* HCO by the photolysis of H_2O in a CO matrix.[5] Among the few examples of applications of these methods to the synthesis of transition-metal complexes are those of $[(olefin)Fe(CO)_4]$[6] and $[Ni(CO)_3(N_2)]$.[7] In this paper we describe the production of a variety of nitrosyl and carbonyl complexes using argon matrices doped with nitrogen oxide and pure carbon monoxide matrices. Preliminary results have been described elsewhere.[8]

EXPERIMENTAL

Cryogenic temperatures were obtained using Air Products AC-3L-110 ' Cryotip ' Joule–Kelvin refrigerators operating with compressed hydrogen gas. I.r. spectra were recorded using Unicam SP 100 and Grubb–Parsons ' Spectromajor ' spectrophotometers which were regularly calibrated with H_2O, DCl, and CO. Band positions are accurate to better than $\pm0{\cdot}5$ cm^{-1}. Samples were deposited on CsBr windows from gas-phase mixtures by the ' pulsed technique.'[9] Argon and CO matrix gases were of B.O.C. Grade ' X ' purity. Nitrogen oxide (Tech. Grade) was purified by passing it through soda lime and a silica gel trap at -80 °C, and ^{13}CO (90%) was obtained from B.O.C. Prochem. The photolysis source was a Philips HPK 125 W medium-pressure Hg arc, water filtered to reduce i.r. heating of the sample.

RESULTS AND DISCUSSION

Reactions.—Pentacarbonyl complex–nitrogen oxide. In solution the complex $[Fe(CO)_5]$ has been shown[10] to react thermally with NO to produce $[Fe(CO)_2(NO)_2]$. The photolysis of the pentacarbonyl complex in an argon matrix doped with 2% NO produced four new i.r. bands in the C–O and N–O stretching region which were identical to those of $[Fe(CO)_2(NO)_2]$ in argon (Table 1). No intermediate carbonylnitrosyl complexes could be detected.

TABLE 1

Product bands (cm^{-1}) in the reaction $[M(CO)_5]$ + NO (Ar matrix) $\longrightarrow$ $[M(CO)_2(NO)_2]$ (M = Fe or Os), compared with those of $[Fe(CO)_2(NO)_2]$ isolated in an argon matrix

$[Fe(CO)_2(NO)_2]$	$[Fe(CO)_5]$ + NO	$[Os(CO)_5]$ + NO
2089m	2088m	2071m
2038s	2038s	2019s
1820m	1816m	1770 *
1787s	1777s †	1729s

* Estimated, as the band is hidden by that due to $(NO)_2$.
† Overlaps with the $(NO)_2$ band.

The above reaction suggested that the hitherto unknown complex $[Os(CO)_2(NO)_2]$ might be prepared analogously. Photolysis of a matrix containing a mixture of $[Os(CO)_5]$,[11] NO, and argon (1 : 30 : 1000) produced free CO, two new terminal carbonyl bands (2071 and 2019 cm^{-1}), and one new terminal nitrosyl band (1729 cm^{-1}). The similarity of these bands to those of the complex $[Fe(CO)_2(NO)_2]$ (Table 1) suggests that $[Os(CO)_2(NO)_2]$ has been produced with the second nitrosyl absorption obscured by the lower of the two $(NO)_2$ bands.[12] The reaction was shown to be reversible by the photolysis of the complex $[Fe(CO)_2(NO)_2]$ in a pure CO matrix. In this case, complete disappearance of $[Fe(CO)_2(NO)_2]$ was observed with the formation of

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† *Present address:* Department of Inorganic Chemistry, School of Chemistry, The University, Newcastle-upon-Tyne NE1 7RU.

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free NO and $[Fe(CO)_5]$. This suggests that in a matrix the four species $[Fe(CO)_5]$, $[Fe(CO)_2(NO)_2]$, NO, and CO reach a steady state during photolysis, and that the position of the steady state can be changed by varying the concentrations of the reactants.

The reaction of the complex $[Fe(CO)_2(NO)_2]$ with CO suggested that other carbonyl species might be produced by photolysis of carbonylnitrosyl complexes and other transition-metal complexes in CO matrices.

Tricarbonylnitrosylcobalt–carbon monoxide. In a CO matrix the high-frequency i.r. spectrum of the complex $[Co(CO)_3NO]$ [Figure 1(*a*)] consists of a high-frequency A_1 CO stretching mode, an E mode split into a doublet by the matrix, and a low frequency A_1 NO stretching mode which is also a doublet. The bands drawn as broken lines in this Figure arise from naturally occurring isotopically substituted CO molecules in the matrix.[13] On photolysis a band due to free NO and two new strong CO stretching bands at 2029·0 and 2011·5 cm^{-1} were produced [Figure 1(*b*)]. The relative intensities of these two bands (1 : 3) were the same in a large number of experiments which included varying the photolysis source, the duration of photolysis, and the matrix ratio of $[Co(CO)_3NO]$ to argon (1 : 500—1 : 15 000). There were no signs of any bands attributable to polynuclear species, except in the most concentrated matrices.

The evidence that the same two bands were always obtained with the same relative intensities, from experiments under a variety of reaction conditions and dilutions, implies that the bands arise from a single mononuclear species. The production of the same species when the complex $[Co_2(CO)_8]$ is photolysed in a CO matrix[14] confirms loss of nitrogen oxide and the formation of the species $[Co(CO)_n]$. In order to identify this species, the complex $[Co(CO)_3NO]$ was photolysed in carbon monoxide matrices containing various concentrations of ^{13}CO (20, 50, and 90%). A total of ten bands were observed (Figure 2), which could be assigned to five levels of ^{13}CO incorporation according to the variation of the relative intensities of the bands with ^{13}CO concentration. This is strong evidence that we have produced the complex $[Co(CO)_4]$, the existence of which has only been inferred previously by e.s.r. studies.[15] Chemically, the formation of the tetracarbonyl complex is very reasonable. A co-ordinatively unsaturated tricarbonyl complex might be expected to take up CO, either on long-wavelength irradiation as does $[Cr(CO)_5]$ to give $[Cr(CO)_6]$,[3] or on warming the matrix, as does $[Ni(CO)_3]$ to give $[Ni(CO)_4]$,[16] but no reaction was observed. Pentacarbonylcobalt would be a 19-electron complex and might lose CO readily on photolysis at a suitable wavelength.

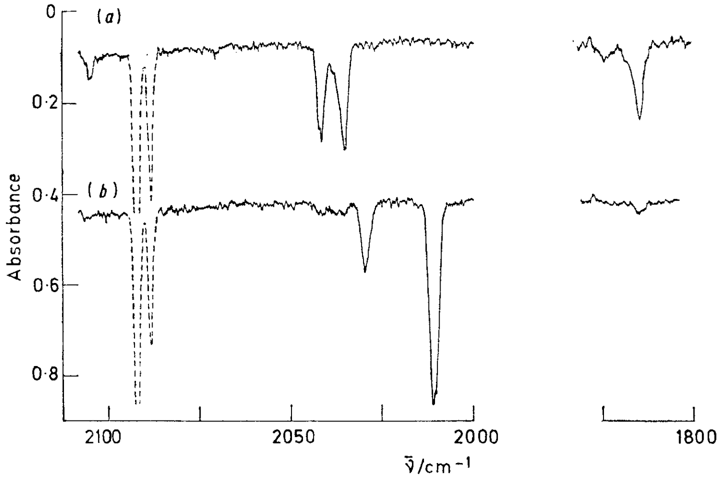

FIGURE 1 I.r. spectrum of the complex $[Co(CO)_3NO]$ in a pure CO matrix at 20 K: (*a*) after deposition; (*b*) after photolysis for 12 min with medium-pressure Hg arc; (- - -), bands due to the matrix itself

A similar separation of the two bands of $[Co(^{12}CO)_4]$ (18 cm^{-1}) was observed when the species was generated both in CO, and in an argon or nitrogen matrix doped with CO (10%), and it is unlikely, therefore, to be simply a matrix splitting, as these are generally smaller (0—10 cm^{-1}) and vary with matrix material.[1] The existence of at least two i.r.-active CO stretching fundamentals, rules out an undistorted tetrahedral geometry for the complex $[Co(CO)_4]$ but is consistent with $D_{2d}(B_2 + E)$ or $C_{3v}(2A_1 + E)$ geometry, provided that in the latter case the higher frequency A_1 is weak and/or obscured by the CO isotope bands. The e.s.r. data[15] also suggested a non-tetrahedral structure. Predictions of the observed isotopic spectra, using a Cotton–Kraihanzel force field[17] and assuming D_{2d} symmetry, consistently reversed the order of some bands and gave band positions with errors of between 2 and 5 cm^{-1}. Assuming C_{3v}

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geometry, however, all observed bands were predicted to within the experimental error (Table 2). Approximate intensity calculations, using C_{3v} geometry and assuming the axial and equatorial bond moments are equal,[17] suggest an angle of *ca.* 100° between the axial and radial CO groups and predict an intensity ratio of approximately 100 : 1 for the two A_1 modes of the complex [Co(^{12}CO)$_4$]. This is consistent with our failure to observe the weaker A_1 mode, which is predicted to be at 2108 cm^{-1}.

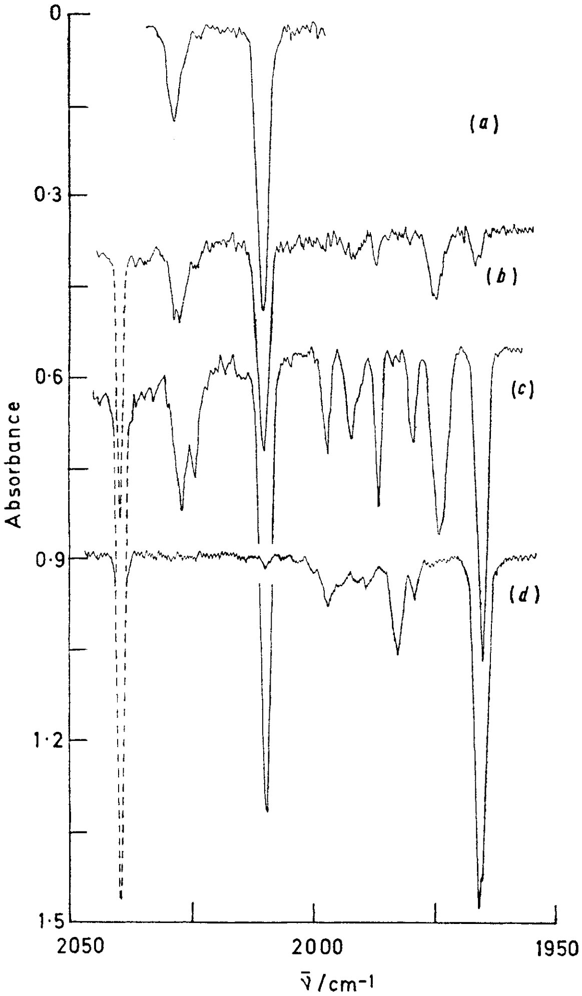

FIGURE 2 I.r. spectra of the complex [Co(CO)$_3$NO] after u.v. photolysis in mixed ^{12}CO–^{13}CO matrices at 20 K: (*a*) pure ^{12}CO; (*b*) 20% ^{13}CO; (*c*) 50% ^{13}CO; (*d*) 90% ^{13}CO; (– – –), ^{13}C^{18}O, natural abundance in the matrix

A priori, one might expect the complex [Co(CO)$_4$] to have a similar structure to that of [Ni(CO)$_4$], which has one more electron and tetrahedral geometry. In carbon monoxide matrices, the T_2 mode of the [Ni(CO)$_4$] complex is split into a doublet, but the splitting in this case is only 6 cm^{-1} and the intensity ratio of the two peaks (2 : 1) suggests an angle very close to that for tetrahedral geometry. It is quite possible, therefore, that both the complexes [Co(CO)$_4$] and [Ni(CO)$_4$] have the same (C_{3v}) structure in CO matrices, but the magnitude of the deviation from tetrahedral geometry for the cobalt complex seems too large to be caused solely by the matrix. Since the electronic ground state of tetrahedral [Co(CO)$_4$](d^9) is $^2T_2$, the molecule is liable to either an E or T_1 Jahn–Teller distortion. If the observed distortion is a Jahn–Teller effect, it provides an interesting contrast to the observed D_{2d} geometry of the d^9 [CuBr$_4$]$^{2-}$ ion.[18] However, the energy difference between the Jahn–Teller distorted C_{3v} and D_{2d} structures may be very small, so that it does not necessarily follow that the [Co(CO)$_4$] complex would adopt a C_{3v} structure in the free state.

TABLE 2

Observed and calculated wavenumbers for isotopically substituted [Co(CO)$_4$] complexes (C_{3v} geometry) with force constants $k_a = 16{\cdot}95$, $k_r = 16{\cdot}76$, $k_{a,r} = 0{\cdot}33$, and $k_{r,r}$ 0·43 mdyn Å^{-1}

			Wavenumber/cm^{-1}	
Complex	Symmetry		Observed	Calc.
[Co(^{12}CO)$_4$]	C_{3v}	A_1		2107·6
		A_1	2029·0 [a]	2029·2
		E	2011·5 [a]	2011·3
[Co(^{12}CO)$_3$(^{13}CO)]	C_s	A'		2099·2
		A'	2028·0 [a,b]	2027·8
		A'	1974·9 [b]	1975·7
		A''	2011·5	2011·3
	C_{3v}	A_1		2099·8
		A_1	1993·6 [b]	1991·3
		E	2011·5	2011·3
[Co(^{12}CO)$_2$(^{13}CO)$_2$]	C_s (2 radial ^{13}CO)	A'		2089·7
		A'	2025·0 [a]	2025·0
		A'	1987·4 [a]	1987·4
		A''	1966·2	1966·4
	C_s (2 radial ^{12}CO)	A'		2089·8
		A'	1993·6 [a,b]	1993·3
		A'	1974·9 [b]	1973·9
		A''	2011·5	2011·3
[Co(^{12}CO)(^{13}CO)$_3$]	C_s	A'		2077·7
		A'	1998·2 [a]	1998·5
		A'	1980·5 [a]	1980·3
		A''	1966·2	1966·4
	C_{3v}	A_1		2078·7
		A_1	2011·5	2011·5
		E	1966·2	1966·4
[Co(^{13}CO)$_4$]	C_{3v}	A_1		2060·6
		A_1	1983·6 [a]	1983·9
		E	1966·2 [a]	1966·4

[a] Wavenumbers used in calculation, giving an average difference between observed and calculated wavenumbers of 0·01%. [b] Bands broadened because of overlap.

Tetracarbonylnitrosylmanganese–carbon monoxide. Photolysis of the complex [Mn(CO)$_4$NO] in a pure CO matrix led to the appearance of two bands in the high-frequency region and the formation of free NO. The reaction did not go to completion and substantial quantities of [Mn(CO)$_4$NO] were left even after photolysis for 5 h.[14,19] The two bands, a strong one at 1989 cm^{-1} and a weaker one at 1996 cm^{-1}, are unrelated as demonstrated by relative intensities. They are presumably due to such carbonyl species as [Mn(CO)$_4$], [Mn(CO)$_5$], and [Mn(CO)$_6$]. The 1989 cm^{-1} band can be obtained

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by photolysis of the complex $[Mn_2(CO)_{10}]$ in a CO matrix;[14] it is worth noting that $[Mn(CO)_6]$ and $[Mn(CO)_4]$ have been postulated as photolysis products of $[Mn_2(CO)_{10}]$ in solution, the former being relatively long-lived.[20] Experiments with ^{12}CO–^{13}CO matrices were difficult to interpret because of bands of $[Mn(^{12}CO)_x(^{13}CO)_{4-x}NO]$ ($x = 1$—4) which obscured vital regions of the spectrum. Thus although the evidence suggests that the 1989 cm^{-1} band may be due to $[Mn(CO)_6]$ the final interpretation must await a study of the reaction of Mn atoms with a CO matrix.

Mechanism.—Photolysis of metal carbonylnitrosyl complexes in inert matrices (*e.g.* argon or methane) generally produces reversible CO loss with no convincing evidence for loss of NO.[14] In isotopically enriched CO matrices, absorptions caused by ^{13}CO substituted nitrosyl complexes grow more rapidly than those of the products involving NO loss. These results could be explained by a lower quantum yield for NO loss compared with that for CO loss and/or a more efficient reversal process for NO. There is also the possibility that loss of nitrogen oxide requires an associative process,[21] and consequently will not take place in the absence of an incoming ligand.

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