Photochemistry of Tricarbonylnitrosylcobalt in Frozen Gas Matrices at 20 K. Infrared Spectroscopic Evidence for Dicarbonylnitrosylcobalt and Dicarbonyl(dinitrogen)nitrosylcobalt

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Infrared evidence is presented for the formation of a three-co-ordinate species, $[Co(CO)_2(NO)]$, on the u.v. photolysis of $[Co(CO)_3(NO)]$ in argon and methane matrices, and for the formation of four-co-ordinate species, $[Co(CO)_2(N_2)(NO)]$ and probably $[Co(CO)(N_2)_2(NO)]$, in nitrogen matrices at 20 K. The primary photolysis steps are readily reversed by irradiation with visible light and by annealing the matrix in the case of the reaction of $[Co(CO)_2(NO)]$ with CO. The results are discussed in relation to the postulate of co-ordinatively unsaturated and expanded-co-ordination-shell species as intermediates in the thermal substitution reactions of $[Co(CO)_3(NO)]$.

THE thermal substitution reactions of the pseudo-$[Ni(CO)_4]$ series of complexes $[M(CO)_{4-n}(NO)_n]$ have been extensively studied.[1] Tetracarbonylnickel undergoes substitution and exchanges CO by a dissociative mechanism, (1), with a first-order rate law (2).[2] The first stage in the decomposition of $[Ni(CO)_4]$ both thermally[3] and photochemically[4] also involves CO loss,

$$[Ni(CO)_4] \xrightarrow[-CO]{\text{slow}} [Ni(CO)_3] \xrightarrow[+L]{\text{fast}} [Ni(CO)_3L] \qquad (1)$$

$$(L = {}^{13}CO, PR_3, \textit{etc.})$$

$$\text{Rate} = k_1[Ni(CO)_4] \qquad (2)$$

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[1] F. Basolo, *Chem. in Britain*, 1969, **5**, 505.

[2] J. P. Day, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1968, **90**, 6927.

[3] J. P. Day, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1968, **90**, 6933.

[4] A. B. Callear, *Proc. Roy. Soc.*, 1962, **A265**, 71.

and it has been suggested that the $[Ni(CO)_3]$ fragment possesses considerable kinetic stability.[1,3,4]

In contrast to the rather simple behaviour of $[Ni(CO)_4]$, the thermal substitution reactions of $[Co(CO)_3(NO)]$ [5,6] and $[Fe(CO)_2(NO)_2]$ [7] follow a two-term rate law (3).

$$\text{Rate} = (k_1 + k_2[\text{L}])\ [\text{nitrosyl complex}] \qquad (3)$$

For ' good ' ligands, *e.g.* PPh_3, at moderate concentration the contribution from the first-order ligand-independent path is negligible, while ' poor ' ligands such as $AsPh_3$ react slowly by a first-order mechanism. The availability of the second-order associative path is generally regarded as a consequence of the ability of the co-ordinated NO molecule to accept additional electron density from the metal atom which can then accommodate the additional ligand, especially if the incoming ligand is a good donor. Rather less is known about the reactivity of the nitrosyl group in these complexes. Since NO may be regarded as a ' three-electron ' ligand, it might be expected to be more strongly bound to the metal than is CO. Up to a point, mass spectroscopy supports this expectation because fragments produced by NO loss are much less abundant than those generated through loss of CO.[8] A kinetic study of the reaction of $[Co(CO)_3(NO)]$ with ^{15}NO has indicated that exchange takes place slowly by a second-order process.[9]

Photolysis of stable molecules in a frozen matrix of an inert gas has been widely used as a method of generating unstable fragments, which are characterised spectroscopically.[10] Such unstable fragments are frequently related to intermediates invoked in mechanistic schemes. Photochemical loss of CO from a metal carbonyl in an inert matrix is now known to be a general phenomenon, *e.g.* in $[Cr(CO)_5]$,[11,12] $[Ni(CO)_3]$,[13] $[Mn(CO)_4H]$,[14] and $[Mn(CO)_3(NO)]$.[15] More recently, anionic metal carbonyl fragments have been produced, *e.g.* $[Cr(CO)_5]^-$ from $[Cr(CO)_6]$ by electron bombardment or photolysis in the presence of sodium atoms [16] and $[Ni(CO)_3]^-$ from $[Ni(CO)_4]$ by vacuum u.v. photolysis.[17] As well as straightforward loss of CO from metal carbonyl complexes, ligand-substitution reactions have also been observed in matrices either by reaction with the matrix, *e.g.* $[Ni(CO)_3(N_2)]$,[18] or with a substrate added to the inert matrix, *e.g.* $[Os(CO)_2(NO)_2]$ [19] and $[Fe(HC{\equiv}CH)(CO)_4]$.[20] In some cases the reactive metal carbonyl fragments are apparently capable of interacting significantly with the ' inert ' matrix, *e.g.* i.r. spectroscopic evidence for $[Fe(CO)_4]\cdots CH_4$ and $[Fe(CO)_4]\cdots Xe$,[21] and shifts of over 100 nm in the visible-absorption maximum of $[Cr(CO)_5]$ depending on the matrix material.[22]

In this paper we describe the production of a variety of species formed from $[Co(CO)_3(NO)]$ in inert (Ar or CH_4) and reactive matrices (N_2) and we relate the findings to the substitution reactions of $[Co(CO)_3(NO)]$.[5,6,9] Preliminary results have been described elsewhere.[23]

EXPERIMENTAL

Cryogenic temperatures (*ca.* 20 K) were obtained using an Air Products AC-3L-110 ' Cryotip ' (a two-stage Joule–Thomson refrigerator capable of achieving 4 K with a combination of hydrogen and helium stages) in the single-stage mode with compressed H_2 gas. Infrared spectra were recorded using a Unicam SP 100 spectrophotometer which was regularly calibrated with water, DCl, and CO. Band positions are accurate to better than ± 0.5 cm^{-1} but have been rounded to the nearest unit. Evacuation (10^{-2} Torr) * of the optical system and cell wells eliminated unwanted background absorption of atmospheric CO_2 and water which result from pathlength inequalities in the sample and reference beams caused by the cryostat. Argon, CH_4, and N_2 matrix gases were of B.O.C. Grade ' X ' purity. The complex $[Co(CO)_3(NO)]$ was obtained from Strem Chemicals Inc. and purified by vacuum distillation. Gas-phase mixtures were made by filling a small volume of a vacuum line (2—20 cm^3) with the vapour pressure of the compound, while maintaining the solid at a particular temperature, and then expanding the contents into an evacuated bulb (1 l). Matrix gas was immediately added to the bulb to give a total pressure of 100—200 Torr and a substrate : matrix gas ratio of between 1 : 5 000 and 1 : 20 000. Provided the matrix gas was added rapidly and in irregular bursts, turbulence within the bulk ensured rapid mixing of the contents. When the diluant gas was added rapidly and the bulb containing the gas mixture was protected from light by wrapping in aluminium foil or by an opaque tape, it could be kept for several hours without deterioration. Samples were deposited on LiF or CsBr windows from gas-phase mixtures by the ' pulsed ' technique.[24]

The photolysis source was a Philips HPK 125-W medium-pressure mercury arc with a water filter (quartz cell; pathlength, 10 mm) to reduce i.r. heating of the sample. Wavelength selection was achieved by a combination of absorbing materials: filter A, $\lambda < 280$, $\lambda > 550$ nm [quartz gas cell (pathlength, 25 mm) containing 3 atm of Cl_2 gas + quartz

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* Throughout this paper: 1 Torr = (101 325/760) Pa; 1 atm = 101 325 Pa.

[5] E. M. Thorsteinson and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 3929.

[6] G. Cardaci, A. Foffani, G. Distefano, and G. Innorta, *Inorg. Chim. Acta*, 1962, **1**, 340.

[7] D. E. Morris and F. Basolo, *J. Amer. Chem. Soc.*, 1968, **90**, 2531, 2536.

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[9] F. A. Palocsay and J. V. Rund, *Inorg. Chem.*, 1969, **8**, 696.

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[11] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, 1962, **84**, 3589; 1963, **85**, 1013.

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[13] A. J. Rest and J. J. Turner, *Chem. Comm.*, 1969, 1026.

[14] A. J. Rest and J. J. Turner, *Chem. Comm.*, 1969, 375.

[15] A. J. Rest, *Chem. Comm.*, 1970, 345.

[16] P. A. Breeze and J. J. Turner, *J. Organometallic Chem.*, 1972, **44**, C7.

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[19] O. Crichton, M. Poliakoff, A. J. Rest, and J. J. Turner, *J.C.S. Dalton*, 1973, 1321.

[20] M. J. Newlands and J. F. Ogilvie, *Canad. J. Chem.*, 1971, **49**, 343.

[21] M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1974, 2276.

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[23] O. Crichton and A. J. Rest, *Proc. 6th Internat. Conf. Organometallic Chem.*, Amherst, Massachusetts, 1973.

[24] M. M. Rochkind, *Spectrochim. Acta*, 1971, **A27**, 547.

gas cell (pathlength, 25 mm) containing 200 Torr of Br_2 gas]; filter B, $\lambda > 400$ nm [quartz gas cell containing Cl_2 gas (as above) + soda glass disc (thickness, 5 mm)]; filter C, $\lambda > 450$ nm (solution of AnalaR $K_2[CrO_4]$ in distilled water with dilution-adjusted cut-on point). Additionally, because of the extreme sensitivity of some of the primary photoproducts (see below) to visible light, it was necessary to remove any visible light from the radiation emitted by the Nernst filament of the i.r. spectrometer.* This was achieved by placing a filter which was opaque to visible and u.v. light between the Nernst source and the sample. The particular germanium interference filter (Ocli Optical Coatings) used for this purpose gave >80% transmission between 2 300 and 1 800 cm^{-1} but caused appreciable tail off in transmission in spectra recorded below 1 800 cm^{-1}.

RESULTS AND DISCUSSION

Photolysis of $[Co(CO)_3(NO)]$ *in Argon and Methane Matrices.*—Preliminary experiments with $[Co(CO)_3(NO)]$ in argon matrices showed that product bands did appear as a result of u.v. photolysis, but that the product was being destroyed by the visible radiation from the Nernst filament of the i.r. spectrometer during the time taken to run a spectrum. In all the experiments in argon and methane matrices described here, the sample was, therefore, protected from visible radiation by using a germanium disk interference filter (see above).

Infrared spectra from an experiment with $[Co(CO)_3(NO)]$ in argon using the germanium filter are shown in Figure 1. At high dilution (1 : 10 000), the spectrum of the parent complex [Figure 1(*a*)] consisted of three strong bands corresponding to the nitrosyl and two terminal carbonyl modes expected for C_{3v} symmetry. Under somewhat higher resolution [Figure 2(*a*)], the two lower wavenumber bands split † at least into doublets [ν(CO) at 2 040 and 2 037 cm^{-1}, ν(NO) at 1 819 and 1 815 cm^{-1}], whilst the upper A_1 terminal CO mode could not be resolved. The two weaker peaks in the starting spectrum [Figure 1(*a*)] are due to $[Co(^{12}CO)_2(^{13}CO)(NO)]$ present at natural abundance.[27]

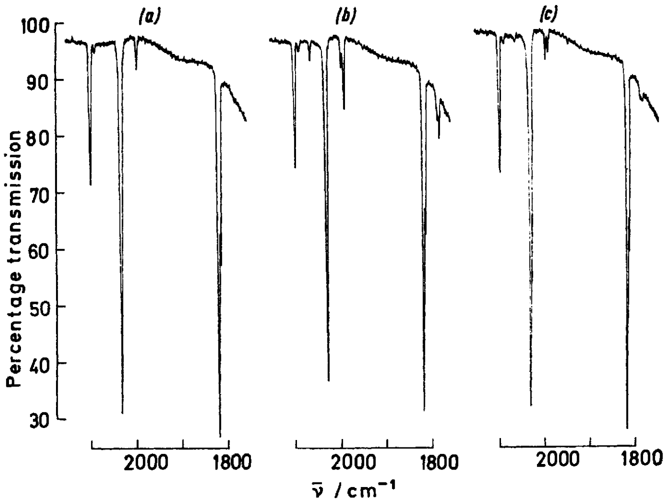

FIGURE 1 Infrared spectra from an experiment with $[Co(CO)_3(NO)]$ isolated in an argon matrix: (*a*) after deposition; (*b*) after 15-min photolysis with u.v. light (filter A); and (*c*) after photolysis for another 10 min with visible light (filter B)

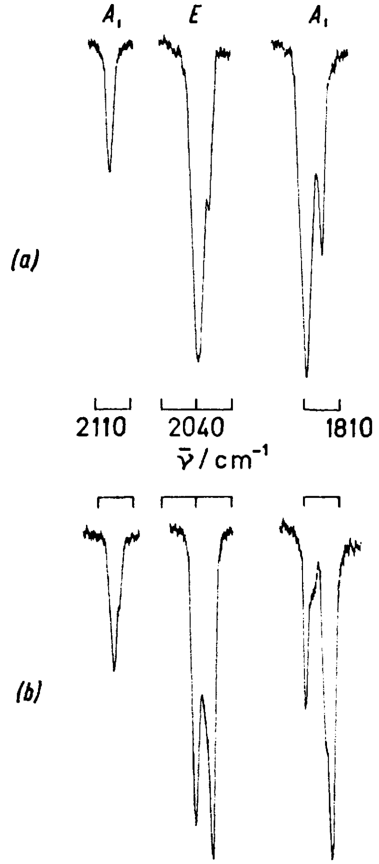

FIGURE 2 High-wavenumber i.r. absorptions of $[Co(CO)_3(NO)]$ under optimum resolution: (*a*) in an argon matrix; and (*b*) in a nitrogen matrix

A brief period of photolysis with a filtered medium-pressure arc (filter A) produced the spectrum in Figure 1(*b*). New terminal CO bands were visible at 2 071 and 1 997 cm^{-1} together with a doublet in the N–O stretching region (1 785 and 1 783 cm^{-1}). With more $[Co(CO)_2(NO)]$ initially present in the matrix, a weak peak due to photochemically generated 'free' CO at 2 138 cm^{-1} was also present,[25] but no other peaks could be detected between 2 150 and 1 200 cm^{-1}. Removal of the Nernst filter (germanium disk) or irradiation with $\lambda > 400$ nm (filter B + Hg arc) caused the original bands to grow at the expense of the product absorptions [Figure 1(*c*)]. Some reversal also occurred on annealing the matrix, *i.e.* the temperature of the matrix was increased briefly to 30—35 K by exerting a 'back pressure' on the liquid-hydrogen coolant and then the matrix was cooled to 20 K before running a spectrum.

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* Experience has shown that this behaviour is very common for unsaturated fragments, *e.g.* $[Fe(CO)_4]$.[25]

† The splittings for the series $[Mo(CO)_{4-n}(NO)_n]$ will be discussed in detail elsewhere.[26]

[25] M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1973, 1351.

[26] O. Crichton and A. J. Rest, unpublished work.

[27] R. S. McDowell, W. D. Horrocks, and J. T. Yates, *J. Chem. Phys.*, 1961, **34**, 530.

In view of the noticeable splitting of the parent nitrosyl band, it is likely that the low-wavenumber product doublet arises from a single nitrosyl fundamental, split by the matrix.[12] The relative intensities of both components of this band, as well as the two new carbonyl absorptions, remained constant under a variety of photolyses, indicating that they arise from a single product species. The dilution used (*ca.* 1 : 10 000) and the reversibility of this reaction rule out any possibility that polynuclear aggregate formation * is involved. All the available evidence identifies the product as the fragment [Co(CO)$_2$(NO)].† The relative intensity of the two terminal carbonyl modes of [Co(CO)$_2$(NO)] is *ca.* 1 : 3, as would be expected [30] for a dihedral angle of 120°. In all probability, therefore, [Co(CO)$_2$(NO)] and [Ni(CO)$_3$] have similar planar geometries.

Figure 3 shows spectra from an experiment with [Co(CO)$_3$(NO)] isolated in a dilute methane matrix (1 : 10 000). Under low resolution the spectra of [Co(CO)$_3$(NO)] in methane [Figure 3(*a*)] and argon [Figure 1(*a*)] were very similar. Spectra at higher resolution, however, revealed minor differences in the exact band positions and splittings in the two matrices (Table 1). Irradiation with the medium-pressure arc and filter A caused new bands to appear [Figure 3(*b*)]. Three of the new bands [marked (1)] are at positions very similar to [Co(CO)$_2$(NO)] in an argon matrix. A weak, but quite reproducible, pair of bands with no counterparts in the argon experiments also appeared at 1 973 and 1 966 cm^{-1} [marked (2)]. On photolysis with visible light (filter B) or on removal of the Nernst filter in the i.r. spectrometer the two weak bands disappeared more rapidly than the principal bands while the parent bands regained their original intensities [Figure 3(*c*)].

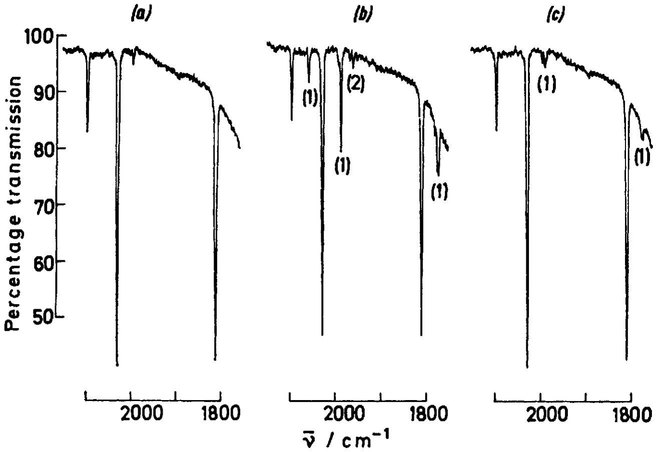

FIGURE 3 Infrared spectra from an experiment with [Co(CO)$_3$(NO)] isolated in a methane matrix: (*a*) after deposition; (*b*) after 5-min photolysis with u.v. light (filter A); and (*c*) after photolysis for another 10 min with visible light (filter B). For an explanation of the numbering of bands (1) and (2) see text

TABLE 1

Positions (cm^{-1}) of bands appearing in experiments with [Co(CO)$_3$(NO)] isolated in argon and methane matrices

	[Co(CO)$_3$(NO)]			[Co(CO)$_2$(NO)]	
	Argon	Methane		Argon	Methane *
$A_1[\nu(CO)]$	2 106	2 103	$A_1[\nu(CO)]$	2 071	2 064
$E[\nu(CO)]$	2 040 2 037	2 035	$B_1[\nu(CO)]$	1 997	1 993
$A_1[\nu(NO)]$	1 819 1 815	1 813 1 810	$A_1[\nu(NO)]$	1 785 1 783	1 781 1 776 1 774

* Other weak bands appeared during photolysis of methane matrices at 1 973 and 1 966 cm^{-1} (see text).

Because of the similarity in the position and intensity of the absorption of [Co(CO)$_2$(NO)] in argon and their counterparts in methane, it is very likely that the major photolysis product of [Co(CO)$_3$(NO)] in a methane matrix is also [Co(CO)$_2$(NO)], which is probably planar. The identity of the other minor product with bands at 1 973 and 1 966 cm^{-1} is not clear. Attempts to generate more of it by using different photolysis sources or by increasing the amount of parent complex present in the matrix (or on the window) were not successful. No other bands could be detected in the N–O stretching region.

Photolysis of [Co(CO)$_3$(NO)] *in Nitrogen Matrices.*‡—The spectrum of [Co(CO)$_3$(NO)] in a pure N$_2$ matrix is shown in Figure 4(*a*). Even under low resolution it was apparent that the A_1 nitrosyl vibration and the E carbonyl vibration are split by the matrix. Under higher resolution [Figure 2(*b*)] the upper A_1 carbonyl vibration at 2 105 cm^{-1} had a detectable shoulder (at *ca.* 2 103 cm^{-1}) and both the E carbonyl vibration and the lower A_1 nitrosyl vibration were clearly resolved into doublets with signs of further unresolved structure (Table 2). The weak peak which is also visible in Figure 4(*a*) is due to a small amount of [Co(^{12}CO)$_2$(^{13}CO)(NO)] present in natural abundance.

Photolysis with the medium-pressure mercury arc and filter A produced the spectrum shown in Figure 4(*b*). In addition to a peak due to free CO (2 139 cm^{-1}), four new bands were visible (1)—(4). All the new bands showed signs of fine splitting under higher resolution (Table 2) but, in view of the splitting of the parent bands, there is no evidence that more than four fundamentals are involved. Irradiation with visible light

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* Early work [13] on the photolysis of [Ni(CO)$_4$] in gas matrices at 20 K was at a dilution of 1 : 200. Under these conditions two new bands (2 065 and 2 016 cm^{-1}, argon matrix) were produced which were assigned to a pyramidal C_{3v} species [Ni(CO)$_3$]. Subsequent work [28] has shown that the intensity of the band at 2 065 cm^{-1} is extremely concentration dependent, and that it does not appear at all for dilutions greater than *ca.* 1 : 2 000. Thus [Ni(CO)$_3$] produced by photolysis has a single band at 2 016 cm^{-1} and is planar in accordance with the co-condensation experiments (Ni atoms with CO and Ar at 4—30 K).[29]

† Experiments with ^{13}CO-enriched [Co(CO)$_3$(NO)] were not attempted because the low yield of product formed by photolysis might result in the bands due to [Co(^{12}CO)(^{13}CO)(NO)] being too weak to observe or being obscured by bands from the range of substituted parent molecules.

‡ The presence of the germanium filter to remove visible radiation from the beam of the i.r. spectrometer had little apparent effect on the outcome of experiments in N$_2$ matrices. It was not used in the experiments which are described in this section.

[28] A. J. Rest, unpublished work.

[29] R. L. Dekock, *Inorg. Chem.*, 1971, **10**, 1205.

[30] L. M. Haines and M. H. B. Stiddard, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 53.

TABLE 2

Positions (cm^{-1}) of bands observed in experiments with [Co(CO)$_3$(NO)] in a pure nitrogen matrix

[Co(CO)$_3$(NO)]		[Co(CO)$_2$(N$_2$)(NO)]		[Co(CO)(N$_2$)$_2$(NO)]	
A_1[ν(CO)]	2 105 2 103	A'[ν(NN)]	2 264 2 256	A'[ν(NN)]	*a*
E[ν(CO)]	2 041 2 036	A'[ν(CO)]	2 072 2 070	A''[ν(NN)]	2 226 2 226
A_1[ν(NO)]	1 820 1 813	A''[ν(CO)]	2 019 2 016	A'[ν(CO)]	2 018 [b]
		A'[ν(NO)]	1 804 1 797	A'[ν(NO)]	1 786 1 782

[a] Too weak to be observed. [b] Estimated as this band is obscured by the A'' mode of [Co(CO)$_2$(N$_2$)(NO)].

(filter B) caused regeneration of the bands of [Co(CO)$_3$(NO)] at the expense of those of the products [Figure 4(*c*)]. Although all the four product bands decreased, it is evident that (1)—(3) do so less markedly than (4) which disappeared entirely. Bands (1)—(3) are probably due to a [Co(CO)$_2$(NO)] moiety and, since its formation involves displacement of CO and the bands are in very different positions from those of [Co(CO)$_2$(NO)] in argon and methane, this is most likely to be [Co(CO)$_2$(N$_2$)(NO)]. Examination of the 2 150—2 400 cm^{-1} region (not illustrated) revealed the expected N–N stretching fundamental as an extremely weak doublet at 2 264 and 2 256 cm^{-1} {*cf.* [Ni(CO)$_3$(N$_2$)], ν(NN) at[18] 2 266 cm^{-1}}.

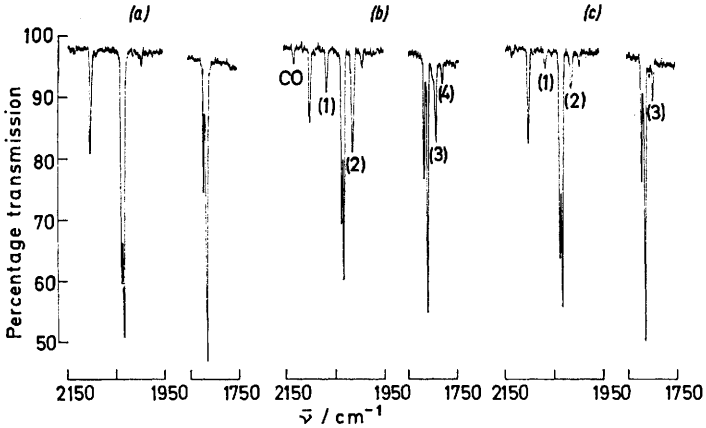


FIGURE 4 Infrared spectra from an experiment with [Co(CO)$_3$(NO)] isolated in a pure nitrogen matrix: (*a*) after deposition; (*b*) after 15-min u.v. photolysis (filter A); and (*c*) after more photolysis for another 20 min with visible light (filter B). For an explanation of the numbering of bands (1)—(4) see text

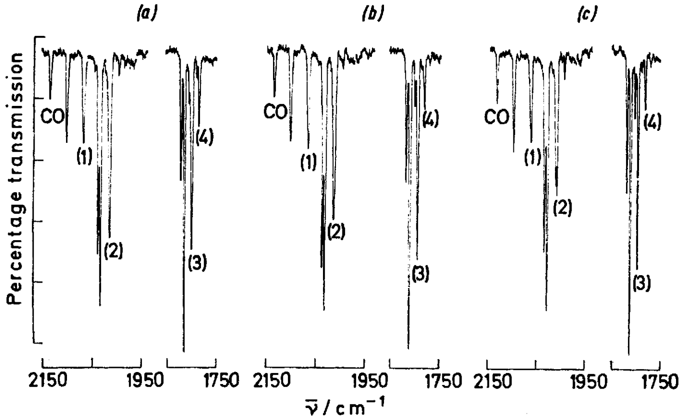


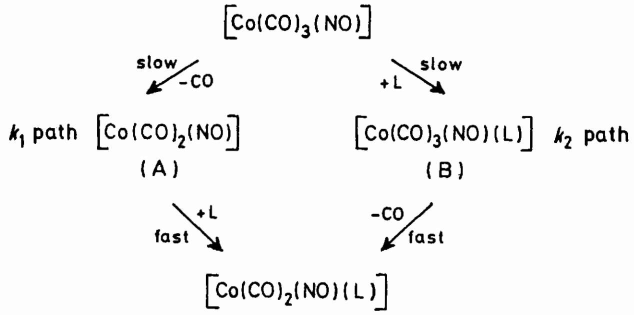
FIGURE 5 Infrared spectra from another experiment with a nitrogen matrix in which more [Co(CO)$_3$(NO)] was present initially: (*a*) after prolonged u.v. photolysis (no filter); (*b*) after further photolysis with visible light (filter C); and (*c*) after annealing the matrix. For an explanation of the numbering of bands (1)—(4) see text

Infrared spectra from another experiment in which more [Co(CO)$_3$(NO)] was deposited in the window are shown in Figure 5. After protracted photolysis with the unfiltered medium-pressure mercury arc, the spectrum shows that substantial amounts of both [Co(CO)$_2$(N$_2$)(NO)] and the species responsible for the other nitrosyl fundamental (4) are present [Figure 5(*a*)]. Brief photolysis with the long-wavelength filter (C) produced the spectrum in Figure 5(*b*) where, although the bands due to the parent complex are unchanged, the intensity of the lower nitrosyl band (4) has decreased. While the slight increase in bands (1) and (3) is consistent with conversion of the second product into [Co(CO)$_2$(N$_2$)(NO)], band (2) had, if anything, decreased.

Despite the position of its NO-stretching vibration {bands (4) at 1 786 and 1 782 cm^{-1}, *cf.* [Co(CO)$_2$(NO)] in argon has A_1 bands at 1 785 and 1 783 cm^{-1}}, the second product cannot be [Co(CO)$_2$(NO)] because it is stable to irradiation by the Nernst beam of the i.r. spectrometer and there is also no corresponding absorption near 1 997 cm^{-1} (Table 1). The anomalous behaviour of band (2) during photolysis with $\lambda > 450$ nm (filter C) suggests that it contains a contribution from a carbonyl vibration belonging to the secondary product, which is probably either [Co(CO)(N$_2$)(NO)] or [Co(CO)(N$_2$)$_2$(NO)]. Some very weak bands were visible in the high-frequency region (2 150—2 400 cm^{-1}) but, although one or more of them may be the corresponding N–N stretching vibration(s), it is not possible to make any convincing assignments. The evidence in favour of assigning the second product as [Co(CO)(N$_2$)$_2$(NO)] is: (*i*) detection of [Co(CO)(N$_2$)(NO)] in experiments without the Nernst filter would be surprising because it would be expected to react with CO in the presence of visible light to give $[Co(CO)_2(N_2)(NO)]$ {*cf.* $[Co(CO)_2(NO)]$ above}; (*ii*) the shift of *ca.* 17 cm^{-1} between band (4) and the nitrosyl band of $[Co(CO)_2(N_2)(NO)]$ (Table 2) is exactly as expected for the replacement of a further carbonyl ligand by N_2 {*cf.* the shift of 16 cm^{-1} between the nitrosyl bands of $[Co(CO)_3(NO)]$ and $[Co(CO)_2(N_2)(NO)]$ and the shift of over 30 cm^{-1} between the nitrosyl bands of $[Co(CO)_3(NO)]$ and $[Co(CO)_2(NO)]$}.

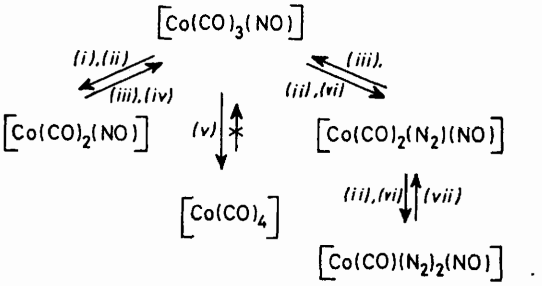
The final spectrum in Figure 5(*c*) demonstrates the effect of annealing the matrix (warming it to *ca.* 35 K and then recooling to 20 K). This process caused little change in the overall intensities of any of the bands, but individual components became sharper and better resolved so that the similarity between the nitrosyl absorptions of $[Co(CO)_3(NO)]$ and the two products was very striking.

Mechanism.—The thermal substitution reactions of $[Co(CO)_3(NO)]$ in solution [5,6,9] can be represented by Scheme 1 involving two paths, k_1 and k_2. Two ' intermediate ' species are invoked, (A) which is co-ordinatively unsaturated and (B) with an expanded co-ordination shell. Both (A) and (B) are likely to be very reactive and it was with this in mind that the matrix-isolation technique was used to endeavour to provide evidence for them or for species closely related to them. Of necessity, care must be taken in extrapolating from matrix-stabilised photolysis products to intermediates in thermal reactions.



SCHEME 1

The reactions of $[Co(CO)_3(NO)]$ in argon and methane matrices show that CO ejection can take place to give a co-ordinatively unsaturated species, $[Co(CO)_2(NO)]$, as a primary photolysis product. The reactivity of $[Co(CO)_2(NO)]$ is demonstrated both by the recombination with CO, when the matrix was irradiated with light of a different wavelength or the matrix was annealed (Scheme 2), and also by the reaction with N_2 to give $[Co(CO)_2(N_2)(NO)]$. No evidence was obtained in this study for NO ejection but, in a separate study, the photolysis of $[Co(CO)_3(NO)]$ in a CO matrix gave $[Co(CO)_4]$ which was characterised by i.r. spectroscopy.[19] The reactions of $[Co(CO)_3(NO)]$ in matrices are summarised in Scheme 2.



SCHEME 2 (*i*) Argon or CH_4; (*ii*) $h\nu$; (*iii*) $h\nu'$; (*iv*) anneal; (*v*) CO, $h\nu''$; (*vi*) N_2; (*vii*) $h\nu'''$

The isolation of $[Co(CO)_2(NO)]$ in argon and methane matrices provides evidence for the photochemical production of (A) (Scheme 1) and thus lends powerful support to its participation in the thermal substitution reactions of $[Co(CO)_3(NO)]$. Like $[Ni(CO)_3]$,[13] the $[Co(CO)_2(NO)]$ fragment is sufficiently reactive to combine with CO at *ca.* 35 K so that the activation-energy barrier to recombination must be very small. Perhaps the interaction of $[Co(CO)_2(NO)]$ and similar species with the solvent may increase the lifetimes of these species in solution.

No evidence was obtained, even in N_2 matrices, for expanded co-ordination-shell species of type (B) (Scheme 1). Similar experiments with $[Mn(CO)(NO)_3]$ did, however, lead to observation of a nitrosyl vibration at *ca.* 1 500 cm^{-1} arising from an unusually bonded nitrosyl ligand.[31] Such a lowering of the nitrosyl band position may result from electron transfer from metal to nitrosyl, possibly accompanied by bending of the M–N–O linkage, thereby creating electron deficiency at the metal atom and a site for attack of a nucleophile, L. It is plausible that a related species is involved in the substitution reactions of $[Co(CO)_3(NO)]$, perhaps as a precursor to (B) (Scheme 1). The fact that such a species has not been observed in matrix-isolation experiments with $[Co(CO)_3(NO)]$ possibly results from an unfavourable overlap of bands in the u.v.–visible spectrum so that no selective source could be found to promote its formation.

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[31] O. Crichton, Ph.D. Thesis, Cambridge, 1975; O. Crichton and A. J. Rest, unpublished work.