Photochemistry of (η-Cyclopentadienyl)nitrosylnickel in Frozen Gas Matrices at 20 K. Infrared Spectroscopic Evidence for Mono- and Di-carbonyl(η-cyclopentadienyl)nickel in Carbon Monoxide Matrices and for a Species formed by Photoionisation or Photoelectron Transfer in Inert Matrices

By **Oliver Crichton** and **Antony J. Rest**,*† University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EP

Infrared evidence, including ^{13}CO data, is presented for the formation of $[Ni(\eta\text{-}C_5H_5)(CO)]$, $[Ni(\eta\text{-}C_5H_5)(CO)_2]$, and ultimately $[Ni(CO)_4]$ on the u.v. photolysis of $[Ni(\eta\text{-}C_5H_5)(NO)]$ in CO or mixed CO and ' inert ' (nitrogen, argon) matrices at 20 K. Infrared evidence, including ^{15}NO data, is also presented for the formation of a species $[Ni(\eta\text{-}C_5H_5)(NO^*)]$ [the asterisk denotes a nitrosyl group with an unusually low value of ν(NO)] on photolysis of $[Ni(\eta\text{-}C_5H_5)(NO)]$ in argon, methane, and nitrogen matrices at 20 K. The significance of the low value of ν(NO) for $[Ni(\eta\text{-}C_5H_5)(NO^*)]$ is discussed in terms of either photoionisation, *i.e.* formation of an ion pair $[Ni(\eta\text{-}C_5H_5)]^+NO^-$, or photoelectron transfer, *i.e.* the nitrosyl group acting as a one- or two-electron ligand instead of a three-electron ligand. It is concluded that $[Ni(\eta\text{-}C_5H_5)(NO^*)]$ belongs to a class of complexes in which electron transfer from the metal to the nitrosyl ligand is particularly extensive and bending of the M–N–O group may be involved. A convenient photochemical synthesis of $[Ni(\eta\text{-}C_5H_5)(^{15}NO)]$ is described.

We have recently described the photochemistry of $[Co(CO)_3NO]$ [1] and $[Fe(CO)_2(NO)_2]$ [2] in low-temperature gas matrices. In inert matrices, *e.g.* argon and methane, the only process which is observed is reversible loss of a CO ligand to give co-ordinatively unsaturated species $[Co(CO)_2(NO)]$ and $[Fe(CO)(NO)_2]$ as in (1). Photoreactions such as (1) have been observed for a wide range of metal carbonyls and substituted metal carbonyls.[3] Photoreactions of nitrosyl complexes in matrices which result in the loss of the nitrosyl ligand have, so far, only been observed in carbon monoxide matrices, *e.g.* conversion of $[Co(CO)_3(NO)]$ and $[Fe(CO)_2(NO)_2]$ into $[Co(CO)_4]$ and $[Fe(CO)_5]$ respectively,[4] presumably because of the photolability of the carbonyl ligand.

$$[Co(CO)_3(NO)] \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} [Co(CO)_2(NO)] + CO \qquad (1)$$

argon at 20 K

The complex $[Ni(\eta\text{-}C_5H_5)(NO)]$ contains a nitrosyl ligand in the absence of any other ligand which can be readily detached photochemically. Although the nitrosyl ligand in this complex shows little tendency to exchange thermally,[5] photolysis of a gas-phase mixture with ^{15}NO causes isotopic exchange and may be used as a convenient means of preparing $[Ni(\eta\text{-}C_5H_5)(^{15}NO)]$ (see Experimental section). Conversion of matrix-isolated $[Ni(\eta\text{-}C_5H_5)(NO)]$ into $[Ni(\eta\text{-}C_5H_5)]$ and free NO thus seemed a likely photochemical process. In this paper we describe the photoreactions of $[Ni(\eta\text{-}C_5H_5)(NO)]$ in ' inert,' *i.e.* argon, nitrogen, and methane, and ' reactive,' *i.e.* carbon monoxide, matrices. Preliminary reports of the work have appeared elsewhere.[6]

---

† *Present address:* Department of Chemistry, The University, Southampton SO9 5NH.

[1] O. Crichton and A. J. Rest, *J.C.S. Dalton*, 1977, 536.

[2] O. Crichton and A. J. Rest, *J.C.S. Dalton*, 1977, 656.

[3] J. J. Turner, *Angew. Chem. Internat. Edn.*, 1975, **14**, 304.

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

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

[6] (*a*) O. Crichton and A. J. Rest, *J.C.S. Chem. Comm.*, 1973, 407; (*b*) O. Crichton and A. J. Rest, *Proc. 6th Internat. Conf. Organometallic Chem.*, Amherst, Massachusetts, 1973.

EXPERIMENTAL

Details of the cryostat, the i.r. spectrometer, the photolysis lamp, matrix gases, and the preparation of gas mixtures with substrate : matrix gas ratios of between 1 : 5 000 and 1 : 20 000 have been given previously.[1] Infrared band positions are accurate to better than ± 0.5 cm^{-1} but have been rounded to the nearest unit. Electronic spectra (u.v.–visible) were obtained with a modified Pye–Unicam SP 1800B spectrometer (modification involved a cut-away sample compartment to accommodate the cryostat, a blackout cloth to eliminate stray light, and a separate E.H.T. switch to activate the photomultiplier in place of the lid switch) and using a LiF cold window with KBr outer windows on the cryostat. Wavelength selection for photolysis was achieved by a combination of the following absorbing materials: filter A, $230 < \lambda < 280$ nm {quartz gas cell containing 3 atm Cl_2 plus quartz solution cells (pathlength, 10 mm) containing AnalaR $Co[SO_4]$ in water and AnalaR $Ni[SO_4]$ in water with cut-on and cut-off points adjusted by dilution}; filter B, $\lambda > 290$ nm [Pyrex-glass disc (3 mm thick)]; filter C, $290 < \lambda < 350$ nm [Pyrex-glass disc (3 mm thick) plus quartz solution cells as in filter A]; and filter D, $\lambda < 280$ and $\lambda > 400$ nm [quartz gas cell (pathlength, 25 mm) containing 3 atm Cl_2 gas].* Additionally, because of the extreme photoreactivity of some of the products 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 using a germanium interference filter (Ocli Optical Coatings Ltd.).[1]

Preparation of $[Ni(\eta\text{-}C_5H_5)(^{15}NO)]$.—A small quartz gas cell (volume, 30 cm^3) was filled with the vapour of $[Ni(\eta\text{-}C_5H_5)(NO)]$ (Strem Chemicals Inc.) at 0 °C. A large excess (*ca.* 100 Torr) of a mixture of ^{14}NO (Matheson Gas Co.; 98%, purified by trap-to-trap distillation) and ^{15}NO (B.O.C. Prochem.; 95% ^{15}NO + 5% ^{14}NO) in the required ratio was added. After photolysis with the medium-pressure lamp for a few minutes the contents of the gas cell were frozen (77 K) and the NO was removed by pumping on the solid held at 193 K with several freeze–pump–thaw cycles (193—273 K) to remove the last trace amounts of NO. Expansion of the ^{15}N-enriched product into a bulb (1 l), followed by dilution with up to 200 Torr of matrix gas, gave a mixture suitable for immediate spray-on.

RESULTS AND DISCUSSION

Reactions.—Photolysis of $[Ni(\eta\text{-}C_5H_5)(NO)]$ *in argon, methane, and nitrogen matrices.* Preliminary experiments with the complex in argon, methane, and nitrogen matrices, using various photolysis sources, produced little evidence for photochemically induced changes. More thorough investigation established that a reaction was occurring but that the product was extremely sensitive to visible radiation. During experiments in these matrices, it was thus necessary to use germanium interference filters to protect the sample from visible light emitted by the Nernst filament of the i.r. spectrometer while spectra were being recorded.[1]

With adequate protection from visible light, even brief exposure to u.v. radiation had a striking effect on samples of $[Ni(\eta\text{-}C_5H_5)(NO)]$ isolated in all the three matrices. Thus in one experiment, irradiation for 1 min of a small amount of a dilute sample of the complex in methane using filter A caused the parent nitrosyl band to decrease in intensity by *ca.* 40%. This change could be completely reversed by photolysis for another 2 min using filter B. Even with conversions to product of this order, no evidence for significant photochemical production of free NO was obtained in any of these matrices, although a band (at *ca.* 1 880 cm^{-1}) [7] would have been readily detectable at the concentrations involved. Similarly, experiments in nitrogen matrices produced no convincing evidence for species of the type $[Ni(\eta\text{-}C_5H_5)(N_2)_x]$, in which the nitrosyl ligand has been replaced by co-ordinated N_2.

The spectra in Figure 1 are taken from an experiment with an extensively ^{15}NO-substituted sample in an argon matrix. Figure 1(*a*) shows the 1 750—1 850 and 1 300—1 400 cm^{-1} regions. In the upper region the nitrosyl absorptions of the two parent species are visible as a pair of triplets. The weak higher-frequency triplet (1 839, 1 835, and 1 830 cm^{-1}) is due to a small amount of unsubstituted $[Ni(\eta\text{-}C_5H_5)(NO)]$, while the intense triplet at lower frequency is due to the preponderance of $[Ni(\eta\text{-}C_5H_5)(^{15}NO)]$. Between 1 400 and 1 300 cm^{-1} a weak broad feature caused by a combination of window and filter effects is visible, but no discrete bands are present.

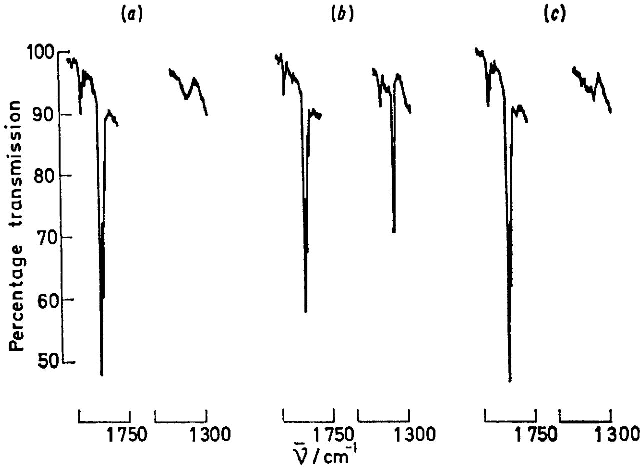

FIGURE 1 Infrared spectra from an experiment in which a mixture of $[Ni(\eta\text{-}C_5H_5)(^{14}NO)]$ and $[Ni(\eta\text{-}C_5H_5)(^{15}NO)]$ was isolated in an argom matrix: (*a*) after deposition; (*b*) after photolysis for 5 min with filter A; (*c*) after more photolysis for another 10 min with filter C

Forward photolysis (filter A) produced the spectrum shown in Figure 1(*b*). Both parent bands are significantly reduced in intensity, and two new bands have appeared between 1 400 and 1 300 cm^{-1}. These bands both appear as doublets under higher resolution (1 392 and 1 390, 1 368 and 1 366 cm^{-1}). The relative intensities of the two bands and their separation of 24 cm^{-1} are exactly as expected for the two isotopic components, arising from an N–O moiety. Photolysis at longer

---

* Throughout this paper: 1 atm = 101 325 Pa; 1 Torr = (101 325/760) Pa; 1 dyn = 10^{-5} N; 1 eV $\approx 1.60 \times 10^{-19}$ J.

[7] W. A. Guillory and C. E. Hunter, *J. Chem. Phys.*, 1969, **50**, 3516.

wavelengths than before (filter C) caused the product bands to disappear completely, while the parent bands were regenerated with a slight change in splitting pattern * [Figure 1(*c*)].

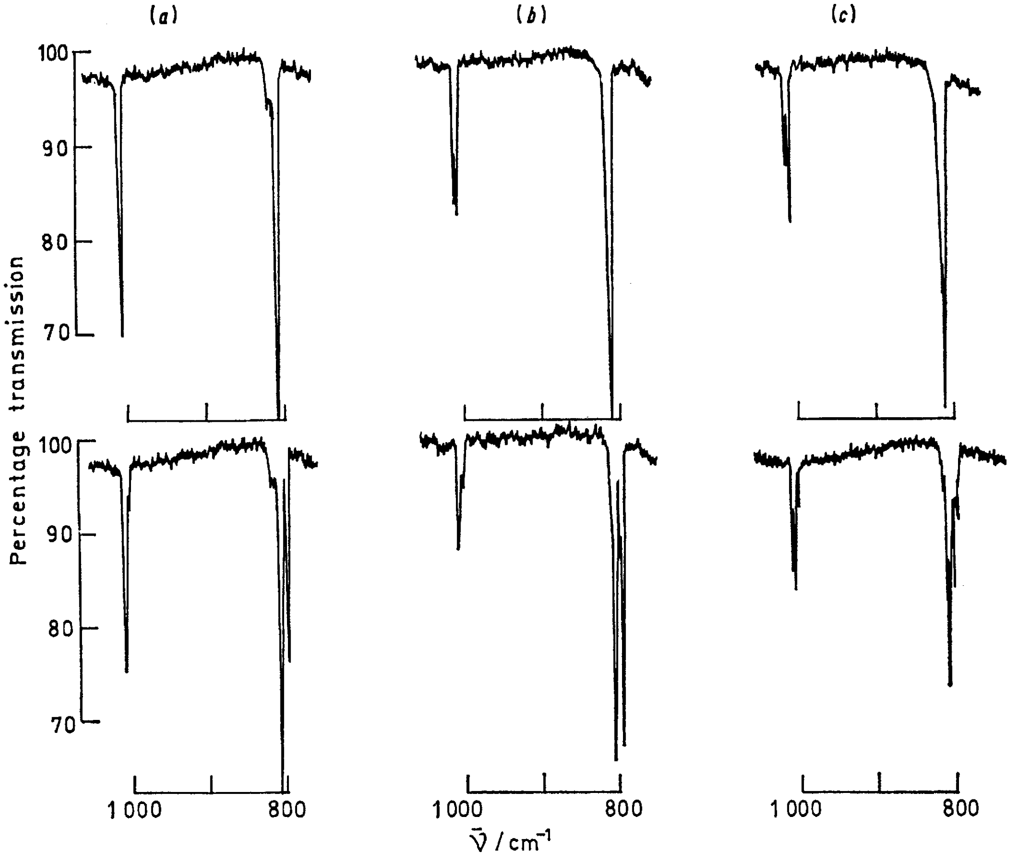

FIGURE 2 Infrared spectra from experiments in which large amounts of [Ni(η-C_5H_5)(NO)] were photolysed in (*a*) argon, (*b*) methane, and (*c*) nitrogen matrices; upper spectra were recorded before photolysis and lower spectra after photolysis with filter A

Similar changes occurred when [Ni(η-C_5H_5)(NO)] was photolysed in methane and nitrogen matrices with new bands appearing in the 1 380—1 390 cm^{-1} region (Table 1). Changes could also be detected in all these matrices in the region of the C–H deformation modes of the parent molecule, although much more sample had to be deposited to produce adequate product absorbance. Unfortunately, the photolysis times with large samples were much longer and the yields were relatively smaller. Figure 2 shows spectra from the 750—1 050 cm^{-1} region from experiments in which a large amount of sample was present. In each of the upper spectra (before photolysis) two relatively strong bands are visible, corresponding to C–H deformation modes of the parent molecule with E_1 and A_1 symmetries [8] (*ca.* 810 and 1 010 cm^{-1} respectively, Table 1). After forward photolysis (lower spectra) new peaks were present to lower frequency of the original bands. In view of the similarity of parent and product spectra in each matrix, it seems likely that a new species containing a co-ordinated η-cyclopentadienyl ligand has been formed.

TABLE 1

Positions (cm^{-1}) of i.r. absorptions observed in experiments with [Ni(η-C_5H_5)(^{14}NO)] in argon, methane, and nitrogen matrices

	[Ni(η-C_5H_5)(^{14}NO)]			[Ni(η-C_5H_5)(^{14}NO*)] [a]		
Matrix	A_1	A_1	E_1			
Argon [b]	1 839	1 010	816	1 392	1 002	797
	(1 802)			(1 368)		
	1 835	1 008	812	1 390	1 000	795
	(1 748)			(1 366)		
	1 830	1 006	804			
	(1 793)					
Methane	1 832	1 008	807	1 385	1 002	801
	1 828	1 005			1 000	799
	1 822					
Nitrogen	1 837	1 009	814	1 388	1 004	802
	1 833	1 005	811		1 000	799
			808			796
			805			

[a] See text for implications of asterisk in NO*. [b] Corresponding data for [Ni(η-C_5H_5)(^{15}NO)] are in parentheses.

Figure 3 compares the u.v. spectra of [Ni(η-C_5H_5)(NO)] in argon before (full line) and after photolysis with filter A (broken line). Despite the broadness of the absorptions and the incomplete conversion, it is obvious

---

* Although the lowest-frequency component of the parent nitrosyl band in argon disappeared slowly on photolysis, it could be regenerated by annealing.

[8] R. D. Feltham and W. E. Fateley, *Spectrochim. Acta*, 1964, **A20**, 1081.

that new absorptions have appeared at slightly longer wavelengths than the intense parent bands at 199 and 283 nm. It is easy to understand why forward photolysis is promoted by radiation with filter A and why irradiation with filter B causes reversal. The shorter-wavelength filter very selectively excites the transition represented by the intense parent band at 283 nm. The second filter isolates the shoulder on the longer-wavelength side of this band due to the product. The spectra also indicate why the yield of product from the complex is limited when large amounts of parent are present. In these circumstances it is impossible to be completely selective with solution filters, so that when a large sample of [Ni(η-C_5H_5)(NO)] is photolysed most of the radiation causing the forward reaction is absorbed by the outer layers of the matrix and the yield of product decreases steadily towards the inner layers.

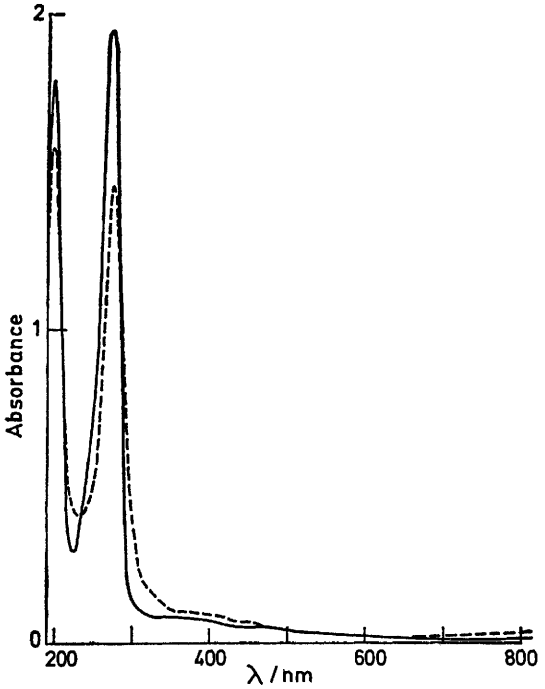

FIGURE 3 Ultraviolet spectra from an experiment with [Ni(η-C_5H_5)(NO)] in an argon matrix before (full line) and after (broken line) photolysis with filter A

Table 1 lists the positions of bands due to [Ni(η-C_5H_5)(NO)] and its photolysis product in argon, methane, and nitrogen matrices. It is difficult to account for a band between 1 390 and 1 380 cm^{-1} as a co-ordinated nitrosyl vibration as it lies completely outside the accepted range for terminal nitrosyl ligands, and nitrosyl-bridged species are excluded by the dilution. Although triply bridging nitrosyl ligands do absorb below 1 400 cm^{-1},[9] formation of polynuclear species would be critically dependent on concentration and would be very slow, if at all, in dilute matrices. In practice, with concentrations of [Ni(η-C_5H_5)(NO)] as low as 1 in 10 000, experiments showed that high dilutions favour rapid and extensive reaction.

Absorptions in the range 1 350—1 373 cm^{-1} have been produced during co-condensation of NO with alkali-metal atoms.[10] Since gas-phase electron-scattering measurements yield a value of 1 355 cm^{-1} for ν(NO) in $[NO]^-$,[11] these bands have been assigned [10] to M^+NO^- ion pairs. Spectroscopically, therefore, it seems plausible [6a] that photolysis of [Ni(η-C_5H_5)(NO)] produces the ion pair $[Ni(\eta\text{-}C_5H_5)]^+NO^-$ (see below).

Photolysis of [Ni(η-C_5H_5)(NO)] *in carbon monoxide matrices*.* Figure 4 illustrates an experiment in which a small amount of the complex was isolated at very high dilution in a pure CO matrix. In Figure 4(*a*) the single intense nitrosyl absorption of the parent molecule can be seen (1 832 cm^{-1}; Table 2) together with some weak bands (marked by asterisks) caused by a trace amount of some impurity in the matrix gas {probably [Fe(CO)$_5$] at *ca.* 0.001%}. Since both [Ni(η-C_5H_5)(NO)] (*ca.* 0.005%) and this impurity are completely isolated, its presence in the matrix can have no effect on the results. The rapid decrease in transmission above 2 050 cm^{-1} is caused by the large amount of CO matrix present.[12]

TABLE 2

Positions (cm^{-1}) of high-frequency i.r. absorptions observed in experiments with [Ni(η-C_5H_5)(NO)] isolated in pure ^{12}CO matrices

	[Ni(η-C_5H_5)(NO)]	[Ni(η-C_5H_5)(NO*)]	Free NO
ν(NO)	1 832	1 386	1 876 (3) [a]
	[Ni(η-C_5H_5)(CO)]	[Ni(η-C_5H_5)(CO)$_2$]	[Ni(CO)$_4$]
ν(CO)	*ca.* 2 070 [b] (1)	2 070 (1) 2 021 (2)	$\left.\begin{matrix}2\,053\\2\,047\end{matrix}\right\}$ (4)

[a] Numbers in parentheses denote particular bands in text and figures. [b] Exact value is uncertain because of overlap with band of [Ni(η-C_5H_5)(CO)$_2$].

Brief photolysis using the unfiltered mercury arc caused a large decrease in the intensity of the parent band and two strong absorptions appeared at 2 070 (1) and 2 021 (2) cm^{-1} [Figure 4(*b*)]. A weak band (4) was also visible at *ca.* 2 050 cm^{-1}. Slightly more prolonged photolysis with the same lamp produced the spectrum in Figure 4(*c*) in which both the original nitrosyl band and the first set of product bands [(1) and (2)] have disappeared while the weak absorption (4) has become a strong doublet. Insufficient sample was present in this experiment for any bands due to the organic part of the molecule to be observed. The positions (2 053 and 2 047 cm^{-1}) and relative intensities of the bands (4) in the final spectrum are very similar to those of the two components of the split T_1 mode of an authentic sample of [Ni(CO)$_4$] isolated in a CO matrix.[13] Photolysis of [Ni(η-C_5H_5)(NO)] in carbon monoxide has thus caused loss of both the nitrosyl and the cyclopentadienyl ligands *via* at least one intermediate.

---

* Germanium filters were not used for experiments in CO matrices because, apart from permitting a weak band at 1 386 cm^{-1} to be observed (*cf.* above), they had no detectable effect on the experimental results.

[9] R. C. Elder, *Inorg. Chem.*, 1974, **13**, 1037.

[10] D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1971, **55**, 3404.

[11] D. Spence and G. J. Schultz, *Phys. Rev.*, 1971, **A3**, 1968.

[12] 'Vibrational Spectroscopy of Trapped Species,' ed. H. E. Hallam, Wiley, London, 1973, p. 57.

[13] R. N. Perutz and J. J. Turner, *J.C.S. Faraday II*, 1973, 452.

Figure 5 shows spectra from an experiment with more complex initially present. Brief irradiation with a filtered mercury lamp (filter D) produced the first spectrum [Figure 5(*a*)]. In addition to a weak band due to ' free ' NO (3), two of the original product bands have appeared, while the intensity of the parent nitrosyl absorption has been reduced by more than 50%. No absorptions due to [Ni(CO)$_4$] are present at this stage. A further short period of photolysis using a different filter (C) produced the spectrum in Figure 5(*b*). The nitrosyl band due to [Ni(η-C$_5$H$_5$)(NO)] has grown, apparently at the expense of the higher-frequency product band (1), while the lower-frequency band (2) is unaffected. A small quantity of [Ni(CO)$_4$] has also been produced (4). More prolonged photolysis with filter C or with B caused further reduction in the intensities of both intermediate bands (1) and (2) while those due to [Ni(CO)$_4$] and [Ni(η-C$_5$H$_5$)(NO)] both grew.

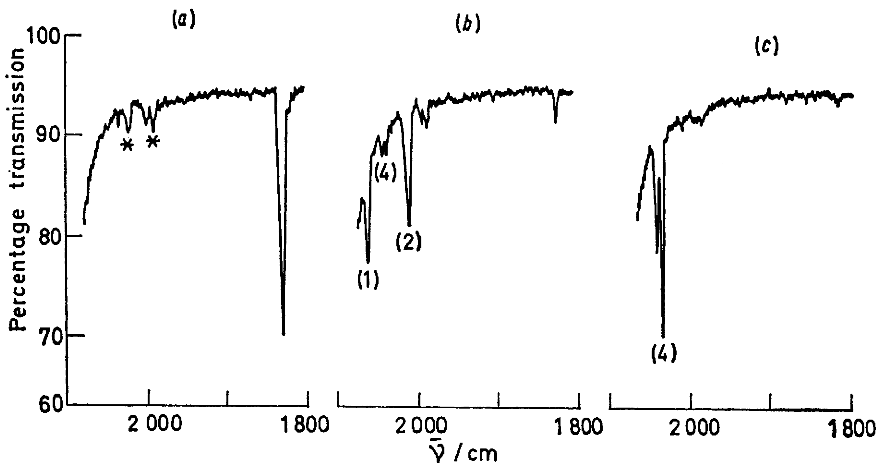

FIGURE 4 Infrared spectra from an experiment with [Ni(η-C$_5$H$_5$)(NO)] isolated in a pure CO matrix: (*a*) after deposition; (*b*) after photolysis for 1 min with the unfiltered Hg arc; (*c*) after photolysis for another 10 min with the same source. The weak bands marked with asterisks are due to a trace amount of impurity in the matrix gas (see text). For an explanation of the numbering of bands (1), (2), and (4) see text

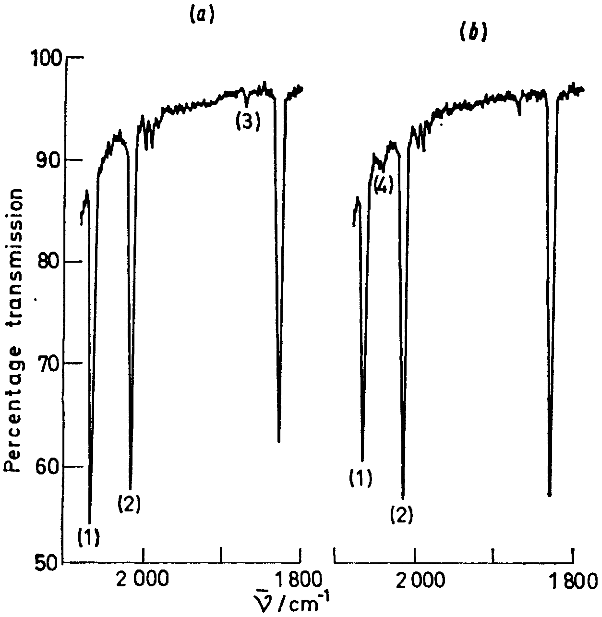

FIGURE 5 Infrared spectra from an experiment with more [Ni(η-C$_5$H$_5$)(NO)] present in the pure CO matrix: (*a*) after photolysis for 5 min with filter D; (*b*) after photolysis for another 2 min with filter C. For an explanation of the numbering of bands (1)—(4) see text

Similar results were obtained in argon or nitrogen matrices containing *ca.* 10% of CO. Bands corresponding to those in pure CO behaved in exactly the same fashion in the mixed matrices although conversion was lower and the formation of [Ni(CO)$_4$] was very slow. No evidence could be obtained in nitrogen-containing matrices for the formation of significant amounts of species containing co-ordinated N$_2$.

Isotopic experiments in pure CO matrices are difficult to interpret as much of the spectral region of interest is obscured by strong matrix absorptions. Instead, a matrix containing 3% of ^{13}CO and 5% of ^{12}CO in nitrogen was used as bands were sharper in this mixture than in other mixed matrices. Photolysis of [Ni(η-C$_5$H$_5$)(NO)] using filter A in this matrix produced a total of five bands, of which two decreased in intensity relative to the others when irradiated with filter C. The simplest explanation for the appearance in ^{12}CO of two bands which behave independently is that they belong to two different monocarbonyl species. This possibility is ruled out, however, by the appearance of more than four bands in the mixed-isotope experiment. As shown in Table 3, the five isotopic bands are consistent with a Ni(CO)$_2$ moiety in which the lower band of the (^{12}CO)$_2$ species overlaps the upper band of the (^{13}CO)$_2$ species. Considering the broadness of the bands and the resulting inaccuracies in their measured positions, the agreement between the observed and calculated spectrum is quite good.

Thus it appears that bands (1) and (2) in Figures 4 and 5 are at least partly due to a single dicarbonyl complex and it is necessary to account for the decrease in intensity of band (1) on photolysis using filter C. Possible explanations are: (*a*) an artefact of the spectrometer caused by inadequate resolution [since the observed half-width of band (1) is more than 4 cm^{-1} for a spectral slit width of just over 1 cm^{-1} this seems unlikely]; (*b*) a change in bond angle (the relative intensities of the two bands of a dicarbonyl moiety are a function of their dihedral angle [14] so that a change of *ca.* 10° would produce the required change in relative intensity); and (*c*) the upper band involves a coincidence [under the highest resolution possible with the available spectrometer, no splitting of band (1) was observed; it did however decrease slightly in half-width (by 0.5 cm^{-1}) during photolysis using filter C].

TABLE 3

Observed and calculated band positions (cm^{-1}) for the $Ni(CO)_2$ moiety in the $[Ni(\eta\text{-}C_5H_5)(CO)_2]$ species produced by photolysis of $[Ni(\eta\text{-}C_5H_5)(NO)]$ in a nitrogen matrix containing 5% of a mixture of ^{12}CO and ^{13}CO

	obs.	calc.[a]
$Ni(^{12}CO)_2$	2 069.6 [b]	2 069.0
	2 019.0	2 018.9
$Ni(^{12}CO)(^{13}CO)$	2 054.2	2 054.8
	1 987.2	1 987.5
$Ni(^{13}CO)_2$	*ca.* 2 020 [b,c]	2 022.9
	1 974.2	1 973.9

[a] Using a Cotton–Kraihanzel force field with $k_{CO} = 16.87$ and $k_{CO,CO} = 0.41$ mdyn $Å^{-1}$. [b] Decreased in intensity relative to the others on photolysis with filter C. [c] Broadened by overlap.

Explanations (*a*) and (*b*) both fail to account for the simultaneous increase in the intensity of the nitrosyl band of $[Ni(\eta\text{-}C_5H_5)(NO)]$, as well as requiring three of the bands in the mixed-isotope experiment to behave similarly to band (1) instead of only two which are actually observed to do so (Table 3). Only the third possibility seems to explain all the observed facts, so that it must be concluded that two species are present after primary photolysis (filter D). Since the mixed-isotope experiment (Table 3) revealed only two bands corresponding to the second product (coincident with the upper bands of the symmetrically substituted dicarbonyls), the second product is almost certainly a monocarbonyl.

A weak band (3) due to liberated NO appeared before any significant quantity of $[Ni(CO)_4]$ was formed, but, except for this band and the others listed in Table 3, no other new bands could be detected between 1 200 and 2 150 cm^{-1}. The inference that neither the mono- nor the di-carbonyl contain co-ordinated NO is confirmed by the formation of small amounts of both species when $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$ (matrix-prepared by subliming the complex and co-condensing with CO gas by slow spraying-on technique [6b]) is photolysed in a CO matrix.

Neither of these intermediate species can be a simple binary carbonyl of nickel as their band positions do not correspond to any of the $[Ni(CO)_x]$ ($x = 1$, 2, and 3) fragments previously reported,[15,16] and it is difficult in any case to believe that such fragments could exist in a pure CO matrix. Since both intermediates are at least partially reconverted into $[Ni(\eta\text{-}C_5H_5)(NO)]$ on photolysis with filter C, no processes involving fragmentation of the cyclopentadienyl ring seem possible. There is also no evidence for reaction of the cyclopentadienyl ligand with CO to give co-ordinated C_5H_5CO as this should absorb at *ca.* 1 850 cm^{-1} (*cf.* HCO).[17] Presumably both intermediates contain a cyclopentadienyl ligand and they are thus $[Ni(\eta\text{-}C_5H_5)(CO)]$ and $[Ni(\eta\text{-}C_5H_5)(CO)_2]$ respectively. The production of $[Ni(\eta\text{-}C_5H_5)(CO)]$ with one less electron than $[Ni(\eta\text{-}C_5H_5)(NO)]$ is not surprising and it is likely that both molecules have similar structures. In contrast, $[Ni(\eta\text{-}C_5H_5)(CO)_2]$ is a '19-electron' complex and it is rather unexpected that it should be the major product of primary photolysis.

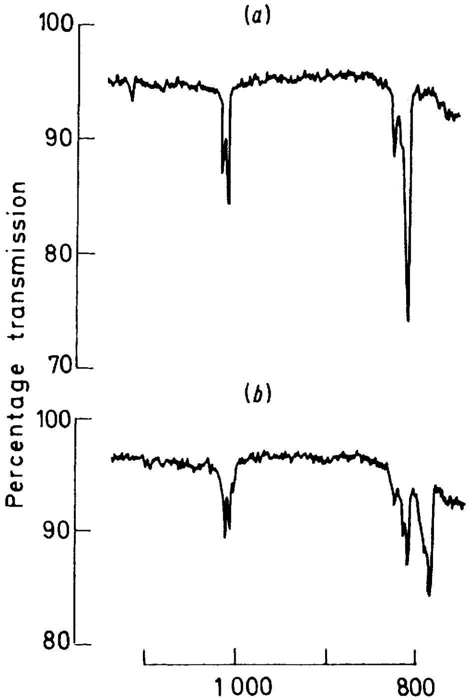

FIGURE 6 Infrared spectra from an experiment in which a large amount of $[Ni(\eta\text{-}C_5H_5)(NO)]$ was present in a pure CO matrix so that some of the C–H deformation bands are visible: (*a*) before and (*b*) after photolysis with filter D

Some of the weak bands associated with the organic ligand in $[Ni(\eta\text{-}C_5H_5)(CO)_2]$ have been observed. In Figure 6 the spectra of $[Ni(\eta\text{-}C_5H_5)(NO)]$ before and after partial conversion into $[Ni(\eta\text{-}C_5H_5)(CO)_2]$ are compared between 1 150 and 750 cm^{-1}. The multiplets at *ca.* 1 016 and 813 cm^{-1} (*cf.* Table 1) in Figure 6(*a*) correspond to C–H deformations of A_1 and E_1 symmetry.[8] As $[Ni(\eta\text{-}C_5H_5)(CO)_2]$ is produced the higher-frequency multiplet broadened and became more complex while a new band appeared at *ca.* 786 cm^{-1}. In view of the similarity between the spectra of $[Ni(\eta\text{-}C_5H_5)(NO)]$ and $[Ni(\eta\text{-}C_5H_5)(CO)_2]$ in this region, it seems likely that the dicarbonyl also possesses an η^5-cyclopentadienyl ligand.

---

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

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

[16] R. L. Dekock, *Inorg. Chem.*, 1971, **6**, 1205.

[17] M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, 1969, **51**, 277.

Although the CO stretching frequencies of $[Ni(\eta\text{-}C_5H_5)(CO)_2]$ are slightly lower than those of $[Co(\eta\text{-}C_5H_5)(CO)_2]$,[6b] the ratio of the intensities of the symmetric and antisymmetric modes are similar in the two cases suggesting that the $M(CO)_2$ moieties have similar geometries. Generally, increasing the number of co-ordinated CO groups in a molecule causes an increase in the value of k_{CO} {*cf.* $[Ni(CO)_x]$}[15] and so it is surprising that k_{CO} for $[Ni(\eta\text{-}C_5H_5)(CO)_2]$ (16.87 mdyn Å^{-1}) is lower than for $[Ni(\eta\text{-}C_5H_5)(CO)]$ 17.31 (mdyn Å^{-1}). If the value for the monocarbonyl is taken as normal in comparison to the value of 17.72 mdyn Å^{-1} derived from the reported C–O stretching frequency of $[Cu(\eta\text{-}C_5H_5)(CO)]$[18] it is necessary to explain why the value for the dicarbonyl should be low. One possibility is that the high-energy orbital which must contain the 19th electron in $[Ni(\eta\text{-}C_5H_5)(CO)_2]$ has a good deal of π^*_{CO} character.

The eventual appearance of $[Ni(CO)_4]$ during photolysis of $[Ni(\eta\text{-}C_5H_5)(NO)]$ in a carbon monoxide matrix suggests that this method could be used to obtain i.r. and u.v. spectra of the cyclopentadienyl radical. Because of the weakness of the i.r. absorptions of this molecule, a very large amount of $[Ni(\eta\text{-}C_5H_5)(NO)]$ would have to be converted into $[Ni(CO)_4]$. Unfortunately, the production of $[Ni(CO)_4]$ is very slow under these circumstances and this experiment has so far not proved possible.

The Significance of the Low-wavenumber Nitrosyl-stretching Frequency: Photoionisation or Photoelectron Transfer?—The appearance of bands at *ca.* 1 390 cm^{-1} (Table 1) on photolysis of $[Ni(\eta\text{-}C_5H_5)(NO)]$ in such relatively inert matrices as argon and methane is reasonably strong evidence for photochemical formation of the ion pair $[Ni(\eta\text{-}C_5H_5)]^+NO^-$. Thermochemical considerations are however less convincing. Small amounts of product were slowly produced even with filters with maximum transmission at *ca.* 500 nm. Although the filters used were not completely selective, it certainly seems probable that the product can be produced by light with a wavelength as high as 400 nm where the available photochemical energy is only *ca.* 3 eV.

A thermodynamic cycle may be drawn for the photoionisation of $[Ni(\eta\text{-}C_5H_5)(NO)]$ in an inert matrix from which it is evident that energy must be supplied to break the Ni–N bond (d.e.) and to ionise the $[Ni(\eta\text{-}C_5H_5)]$ fragment. At the same time, the addition of an electron to NO (—e.a.) and the interaction between the two ions $(-e^2/\varepsilon R)$ liberate energy. Since the entropy terms must be negligible at the low temperatures involved we obtain (2). Assuming reasonable values for the parameters involved, *i.e.* —d.e. $\simeq$ 1.5 eV, i.p. $\simeq$ 7.5 eV

$$\Delta G \simeq \Delta H = \text{d.e.} + \text{i.p.} - \text{e.a.} - (e^2/\varepsilon R) \qquad (2)$$

(ionisation potential of nickel), e.a. $\leqslant$ 1 eV (a maximum estimate),[11] and $(e^2/\varepsilon R) \leqslant 4$ eV (*cf.* the strength estimated for an ionic bond in monomeric KBr [19]), ΔG must be at least +4 eV. Since the photochemical energy required for reaction is apparently only 3 eV, this reaction is not feasible as a single-stage process unless there is either residual covalent interaction between the ions or there is some reason why $[Ni(\eta\text{-}C_5H_5)]^+$ is a particularly stable ion (*i.e.* i.p. < 7.5 eV).

$$\begin{tikzcd}
{[Ni(\eta\text{-}C_5H_5)(NO)]\ (\text{matrix})} \arrow[r, "\Delta H"] & {[Ni(\eta\text{-}C_5H_5)]^+NO^-\ (\text{matrix})} \\
{[Ni(\eta\text{-}C_5H_5)](g) + NO(g)} \arrow[u, "\text{d.e.}"'] \arrow[r, "\text{i.p.} - \text{e.a.}"] & {[Ni(\eta\text{-}C_5H_5)]^+(g) + [NO]^-(g)} \arrow[u, "-e^2/\varepsilon R"']
\end{tikzcd}$$

Supporting evidence for the second possibility comes from the mass spectra of the sandwich compounds $[M(\eta\text{-}C_5H_5)_2]$ (M = Ni, Co, or Fe) in which the $[Ni(\eta\text{-}C_5H_5)]^+$ fragment is particularly abundant relative to the molecular ion.[20] Two factors may contribute to an unusually low ionisation potential for $[Ni(\eta\text{-}C_5H_5)]$. First, if one regards the neutral molecule and cation as $C_5H_5^-$ bound to Ni^+ and Ni^{2+} respectively, electron donation from ligand to metal will be particularly favourable in the latter case, leading to a strengthened metal–ligand bond. The second factor arises from ligand-field considerations. For $[Ni(\eta\text{-}C_5H_5)]$ with the metal in a C_{5v} field, the *d* orbitals transform as $a_1(d_{z^2}) + e_1(d_{xz},d_{yz}) + e_2(d_{x^2-y^2},d_{xy})$. Because of the distribution of charge, orbitals directed principally along the *z* axis will have high energies so that possible configurations are $e_2{}^4e_1{}^4a_1$ or $e_2{}^4a_1{}^2e_1{}^3$. In either case, loss of an electron from the highest energy level to give $[Ni(\eta\text{-}C_5H_5)]^+$ ($e_2{}^4,e_1{}^4$ or $e_2{}^4,a_1{}^2e_1{}^2$) should be relatively favourable.

If photoionisation is not the correct explanation for the appearance of N–O stretching vibrations at *ca.* 1 390 cm^{-1}, the most likely alternative is that an extreme case of electron transfer to the nitrosyl ligand is involved. {An isonitrosyl complex $[Ni(\eta\text{-}C_5H_5)(ON)]$ is also conceivable although no satisfactory precedent exists for this type of structure.} A number of other low-wavenumber nitrosyl absorptions (1 400—1 500 cm^{-1}) have been observed in experiments with $[Mn(CO)(NO)_3]$, $[Mn(CO)_4(NO)]$, and $[Cr(NO)_4]$ isolated in inert-gas matrices.[21] Presumably these bands arise from a range of complexes in which progressively more electron density is transferred to the nitrosyl π^* orbitals and the example

---

[18] F. A. Cotton and R. J. Marks, *J. Amer. Chem. Soc.*, 1970, **92**, 5114.

[19] M. Karplus and R. N. Porter, 'Atoms and Molecules,' W. A. Benjamin, New York, 1970, p. 263.

[20] J. Müller and L. D'or, *J. Organometallic Chem.*, 1967, **10**, 313.

[21] O. Crichton, Ph.D. Thesis, University of Cambridge, 1975; O. Crichton and A. J. Rest, *J.C.S. Dalton*, in preparation.

recorded in this paper may represent the extreme limit of a spectrum of values.

At this stage it seems appropriate to formulate the new nitrosyl species as [Ni(η-C_5H_5)(NO*)], one of a class of [ML_n(NO*)] complexes where the asterisk denotes a nitrosyl ligand where electron transfer has occurred to an unusually large extent (no excited state is implied). Consequences of such electron transfer from metal to nitrosyl are (*a*) the metal atom would be relatively electron deficient and hence susceptible to nucleophilic ligand attack, and (*b*) the nitrosyl ligand may become progressively more bent [22] as more electron density is transferred to it. Future work will attempt to investigate further the nature of the M(NO*) bonding.

We thank the S.R.C. together with I.C.I. Ltd., Petrochemicals Division, Billingham, for the award of a C.A.P.S. Studentship (to O. C.), and the Royal Society for support (grant to purchase the Pye–Unicam SP 1800B spectrometer) and for the award of a Pickering Research Fellowship (to A. J. R.).

[6/1563 *Received, 9th August, 1976*]

---

[22] For a recent review including discussion of linear *versus* bent co-ordination of the M–N–O group see J. H. Enemark and R. D. Feltham, *Co-ordination Chem. Rev.*, 1974, **13**, 339.