Photochemistry of Dicarbonylcyclopentadienylcobalt in Frozen Gas Matrices at 12 K. Infrared Spectroscopic Evidence for Tricarbonylcyclopentadienylcobalt and Carbonylcyclopentadienyl(dinitrogen)cobalt Complexes

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Infrared spectroscopic evidence, including ^{13}CO labelling and energy-factored CO force-field fitting, is presented to show that on photolysis of [Co(η^5-C_5H_5)(CO)$_2$] at high dilution in CO and N_2 matrices at 12 K new species [Co(η^3-C_5H_5)(CO)$_3$] and [Co(η^5-C_5H_5)(CO)(N_2)] are produced. No evidence has been found for the formation of [Co(η^5-C_5H_5)(CO)] and CO on photolysis of [Co(η^5-C_5H_5)(CO)$_2$] at high dilution in the inert matrices of Ar and CH_4. The *reversibility* of the reaction [Co(η^5-C_5H_5)(CO)$_2$] + CO $\rightleftharpoons$ [Co(η^3-C_5H_5)(CO)$_3$] is interpreted as confirming the existence of an expanded-co-ordination-number species as the intermediate in the substitution reactions of [Co(η^5-C_5H_5)(CO)$_2$]. This is the *first* time that an expanded-co-ordination-number species, corresponding to an intermediate proposed in an associative mechanism, has been observed by matrix-isolation studies. At low dilutions, photolysis of [Co(η^5-C_5H_5)(CO)$_2$] in Ar, CH_4, and N_2 matrices is shown to produce [{Co(η^5-C_5H_5)(CO)}$_2$] and this is supported by ^{13}CO labelling and energy-factored CO force-field fitting together with comparison with the matrix i.r. spectrum of ^{13}CO-enriched [{Ni(η^5-C_5H_5)(CO)}$_2$].

IT has been reported that CO exchange with [Co(η-C_5H_5)(CO)$_2$] [1,†] and [Co_2(CO)$_8$] [2] is extremely rapid at 25 °C and is much faster than CO exchange with the corresponding simple metal and arenemetal carbonyls of Fe, Mn, and Cr. However, although CO exchange with [Co_2(CO)$_8$] has been shown to proceed by a dissociative mechanism,[2] exchange of CO with [Co(η-C_5H_5)(CO)$_2$] clearly involves a first-order dependence on the CO concentration, *i.e.* a bimolecular S_N2 associative mechanism.[1] In carbonylcyclopentadienylmetal complexes the nature of the bonding between CO and the metal is essentially the same as that in simple metal carbonyls,[3] therefore, the first-order dependence on the CO concentration for [Co(η-C_5H_5)(CO)$_2$] must be due to the cyclopentadienyl ring playing a direct part in the exchange mechanism. It has been suggested [4] that the presence of the cyclopentadienyl ring allows the transfer of electron density from the metal to the ring, *i.e.* an equilibrium [see (1)]. This would make the metal electron-deficient and therefore it would be susceptible to attack by a nucleophile, *e.g.* CO or PR_3.

$$[(\eta^5\text{-}C_5H_5)Co(CO)_2] \rightleftharpoons [(\eta^4\text{-}C_5H_5)^-Co^+(CO)_2] \quad (1)$$

A recent study of the photolysis of [Co(η-C_5H_5)(CO)$_2$] at −78 °C in a light petroleum solution swept by a slow stream of N_2 has demonstrated the formation of an unstable species with a single terminal CO-stretching band at 1 970 cm^{-1}. It has been proposed [5] that the primary photoprocess is the loss of a CO ligand to form the unstable unsaturated monocarbonyl, [Co(η-C_5H_5)(CO)], and that this species is the intermediate in the formation of a number of di- and tri-nuclear complexes [5] and also in the catalysis of the polymerisation of alkynes.[6] The primary step after generation of [Co(η-C_5H_5)(CO)] is formation of the mixed mononuclear complex [Co(η-C_5H_5)(CO)(RC≡CR)] [6] which reacts further, either thermally or photochemically, with excess of alkene to give a variety of substituted cyclobutadiene and cyclopentadienone complexes [7] plus the corresponding hexasubstituted benzene.[7,8] However, the formation of any substituted complex, *e.g.* [Co(η-C_5H_5)(CO)(PPh_3)] or [Co(η-C_5H_5)(CO)(RC≡CR)], from the monocarbonyl species [Co(η-C_5H_5)(CO)] seems to be at variance with the kinetic study mentioned earlier.[1]

It has been shown that the matrix-isolation technique is an extremely powerful tool for investigating photochemical reactions and for characterising reactive species.[9] A variety of different carbonylmetal complexes has been investigated where ligand exchange takes place by purely dissociative mechanisms,[9] including ejection of bulky ligands from complexes,[10] as, for example, in equation (2) where L = pyridine, 3-bromopyridine, or H_2S. There have been no reports of expanded-co-ordination-number species, such as are proposed in associative mechanisms, in matrices and therefore we undertook a matrix-isolation study of the photochemical behaviour of [Co(η-C_5H_5)(CO)$_2$] in inert (Ar, CH_4) matrices and in reactive (CO, N_2) matrices. We relate the results to the apparent discrepancy between kinetic studies, which indicate an associative path, and low-temperature solution photochemical studies, which indicate a dissociative path.

$$[W(CO)_5L] \xrightarrow[\text{Ar or } CH_4 \text{ matrices}]{h\nu \text{ at } 12 \text{ K}} [W(CO)_5] + L \quad (2)$$

EXPERIMENTAL

Cryogenic temperatures (*ca.* 12 K) were obtained using a closed-cycle helium refrigeration system (Air Products and Chemicals Inc. Displex CSA-202). Matrices were prepared by making gas mixtures of the complex and matrix gas of the required composition (1 : 2 000—5 000), using a vacuum line and standard manometric techniques, and depositing the gas mixture on to the cooled CsI window by the ' pulsed ' technique.[11] The pulsing volume was 10 cm^3 and the pulsing pressure was in the range 80—150 Torr,‡ *i.e.* 0.05—0.09 mmol of gas per pulse, and typically 20—30 pulses of [Co(η-C_5H_5)(CO)$_2$] in host matrix gas mixtures were

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† Where η is not superscripted it is implied that all skeletal C atoms of the ligand are bound to the metal, *i.e.* η^4-C_4H_4, η^5-C_5H_5, and η^6-C_6H_6.

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

deposited to give transparent matrices. The complex $[\{Ni(\eta-C_5H_5)(CO)\}_2]$ was not volatile enough to prepare matrices by the pulsed technique and matrices of this complex were prepared by heating a sample to 50 °C and slowly co-depositing the vapour with a stream of matrix gas.

Infrared spectra were recorded on a Grubb Parsons Spectromajor grating spectrometer modified to have a grating change at 1 850 rather than at 2 000 cm^{-1}. Calibration in the CO-stretching region was regularly carried out using the gas-phase absorptions of DCl, CO, and H_2O. Resolution was better than 1 cm^{-1} and reproducibility of measurement was ± 0.5 cm^{-1}.

The photolysis source was a Philips HPK 125-W medium-pressure mercury lamp. Wavelength-selective photolysis was achieved by a combination of absorbing materials: filter A, $\lambda < 280$ and > 550 nm, quartz gas cell (pathlength 25 mm) containing Cl_2 (2 atm) + quartz gas cell (pathlength 25 mm) containing Br_2 (200 Torr); filter B, $\lambda > 290$ nm, Pyrex glass disc (thickness 5 mm).

TABLE 1

Band positions (cm^{-1}) for $[Co(\eta^5-C_5H_5)(CO)_2]$ and its photoproducts in various matrices at 12 K

Complex		CO		N_2	Ar	CH_4
$[Co(\eta^5-C_5H_5)(CO)_2]$	ν(CO)	2 032.1 1 971.9		2 034.7 1 974.6	2 032.8 1 971.0	2 029.1 1 967.9
	ν(ring)	817.3		814.8	816.5	814.9
$[Co(\eta^3-C_5H_5)(CO)_3]$	ν(CO)	2 075.0 2 018.0				
	ν(ring)	780.9				
$[Co(\eta^5-C_5H_5)(CO)(N_2)]$			ν(CO)	1 981.9		
			$\nu(N_2)$	2 164.6		
			ν(ring)	806.3		
$[\{Co(\eta^5-C_5H_5)(CO)\}_2]$			ν(CO)	1 798.9	1 794.4	1 791.2

Matrix gases (Ar, CH_4, CO, and N_2) were of grade 'X' purity and obtained from B.O.C. Ltd. Enriched ^{13}CO (95%) and $^{15}N_2$ (99%) were obtained from B.O.C. Prochem Ltd. The compounds $[Co(\eta-C_5H_5)(CO)_2]$ and $[\{Ni(\eta-C_5H_5)(CO)\}_2]$ were obtained from Strem Chemicals Inc. and the former was redistilled and dried over P_2O_5 before use. Matrices containing ^{13}CO-enriched $[Co(\eta-C_5H_5)(CO)_2]$ were obtained by making the matrix mixture with a ^{12}CO–^{13}CO gas mixture of known composition in a quartz bulb and photolysing the gas sample prior to deposition. Samples of ^{13}CO-enriched $[\{Ni(\eta-C_5H_5)(CO)\}_2]$ were obtained by stirring a solution of the complex overnight in cyclohexane (Spectrosol, Hopkins and Williams Ltd.) at 25 °C in a ^{12}CO–^{13}CO atmosphere of known composition and then pumping off the gas and solvent and subliming the solid.

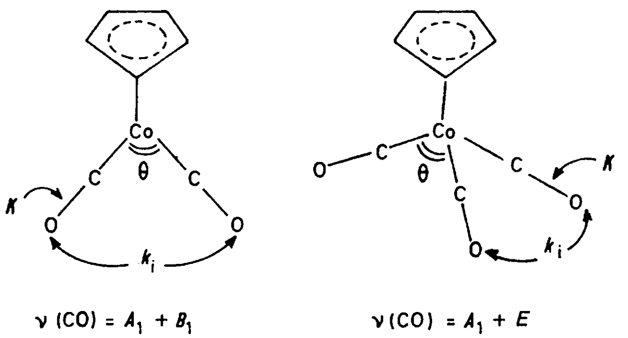
RESULTS

Photolysis of $[Co(\eta-C_5H_5)(CO)_2]$ *in* CO *Matrices*.—The i.r. spectrum of $[Co(\eta-C_5H_5)(CO)_2]$, isolated in a pure CO matrix at a dilution of 1 : 2 000, in the terminal CO-stretching and ring-deformation regions is shown in Figure 1(*a*). The two terminal CO-stretching bands (2 032.1 and 1 971.9 cm^{-1}) correspond to the two modes (A_1 and B_1) expected for a molecule with C_{2v} local symmetry for the CO ligands.[12] The observed relative intensity of the two terminal CO bands (0.87 for $A_1 : B_1$ and obtained by tracing and weighing the bands) was used to calculate a OC–M–CO angle of 94.0 ± 1.0°,* which is in good agreement with solution (96°) [13] and electron-diffraction (98.6°) [14] results and those for a series of co-ordinatively unsaturated $[ML(CO)_2]$ species [100°; ML = $Cr(\eta-C_6H_6)$, $Mn(\eta-C_5H_5)$, or $Fe(\eta-C_4H_4)$].[12]

Irradiation of the matrix with the filtered medium-pressure mercury arc (filter A) produced the i.r. spectrum shown in Figure 1(*b*). Destruction of the parent molecule is accompanied by the growth of new bands in the terminal CO-stretching region (2 075.0 and 2 018 cm^{-1}, Table 1) and a weaker new band in the ring-deformation region (780.9 cm^{-1}). After irradiation with the visible-region output of the mercury arc lamp (filter B) the new product bands were observed to decrease with the regeneration of $[Co(\eta-C_5H_5)(CO)_2]$ bands [Figure 1(*c*)]. The relative intensity of the new terminal CO-stretching bands (0.27 for 2 075 and 2 018 cm^{-1} bands) remained constant under a variety of photolysis conditions (time and radiation) indicating that the bands arose from a single product species. The dilution used (*ca.* 1 : 2 000—5 000) and the reversibility of the matrix reaction rule out the possibility of formation of polynuclear aggregate species.

In order to establish the structure of a matrix-isolated species it is necessary to be able to match the observed and calculated i.r. spectra for a range of ^{13}CO-enriched molecules in respect of the number of bands and their positions and the relative intensities of the bands for a given ^{13}CO composition. The calculation of frequencies and corresponding intensities for a typical predicted spectrum used a CO-factored force-field method,[15] which neglects *G* and *F* matrix coupling between CO-stretching modes and other molecular vibrations and, since no CO group has a common atom with any other CO group in the molecule, all 'off-diagonal' elements of the *G* matrix are also zero. The use of the CO-factored force-field method usually needs certain force-constant approximations to be made [16] because of the overdetermined nature of the problem under consideration. In the cases of $M(CO)_2$ and $M(CO)_3$ fragments with local C_{2v} and C_{3v} geometries respectively, however, the systems are exactly determined and no assumptions are necessary.

The i.r. spectrum of $[Co(\eta-C_5H_5)(CO)_2]$, enriched with *ca.* 60% ^{13}CO, in the terminal CO-stretching region is shown



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* Bond angles calculated from relative intensities using the standard expressions $I_{sym}/I_{antisym} = \cot^2(\theta/2)$ and $[3\cot^2(\theta/2) - 1]/4$ for $M(CO)_2$ and $M(CO)_3$ species respectively.

in Figure 2(*a*). Defining the structural parameters and force constants as below led to the observed and calculated band positions given in Table 2. The calculations give an excellent fit of the observed band positions for [Co(η-C_5H_5)(CO)$_2$] with a mean error * of 0.32 cm^{-1} and a maximum error measured as 0.7 cm^{-1}. A period of photolysis with filter A produced a number of new bands [Figure 2(*b*)]. Force constants obtained from the unenriched photoproduct, assuming a C_{3v} Co(CO)$_3$ fragment, were used to

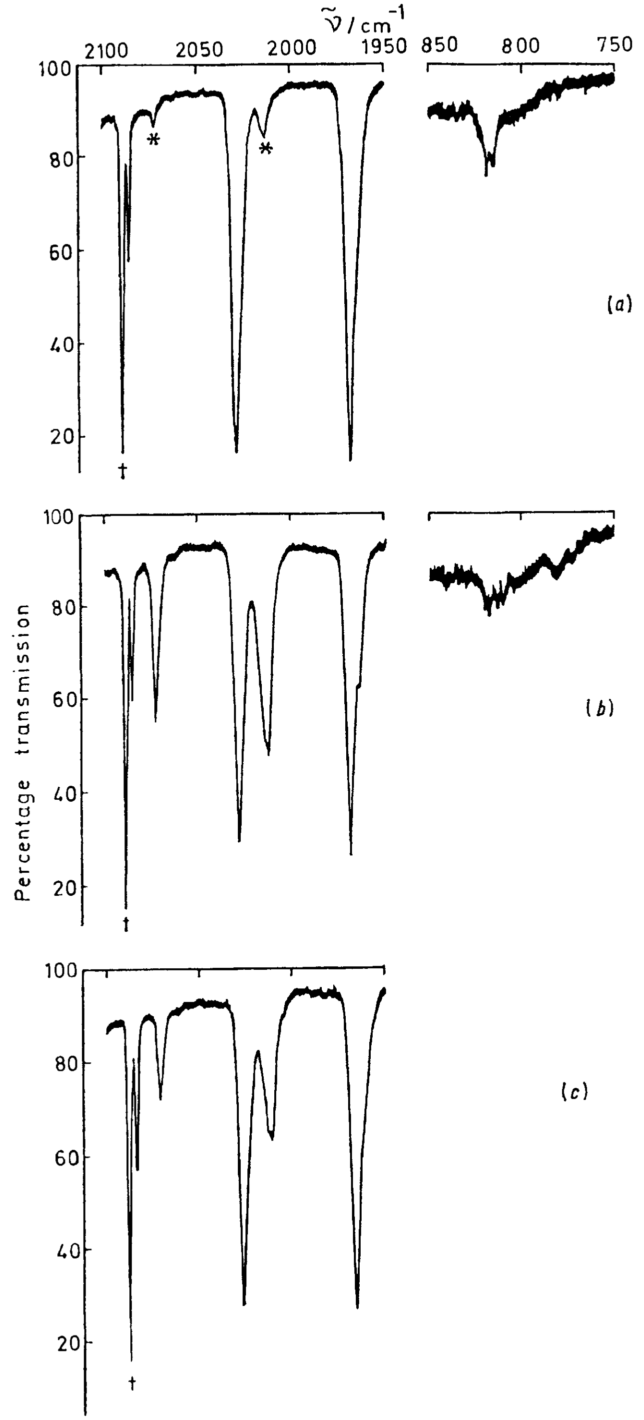

FIGURE 1 Infrared spectra from an experiment with [Co(η-C_5H_5)(CO)$_2$] isolated at high dilution in a CO matrix: (*a*) after deposition, (*b*) after photolysis for 15 min using filter A, and (*c*) after photolysis for another 15 min using filter B. Bands marked † are due to CO isotopes in the host matrix and those marked * in (*a*) are due to photolysis by the Nernst glowbar

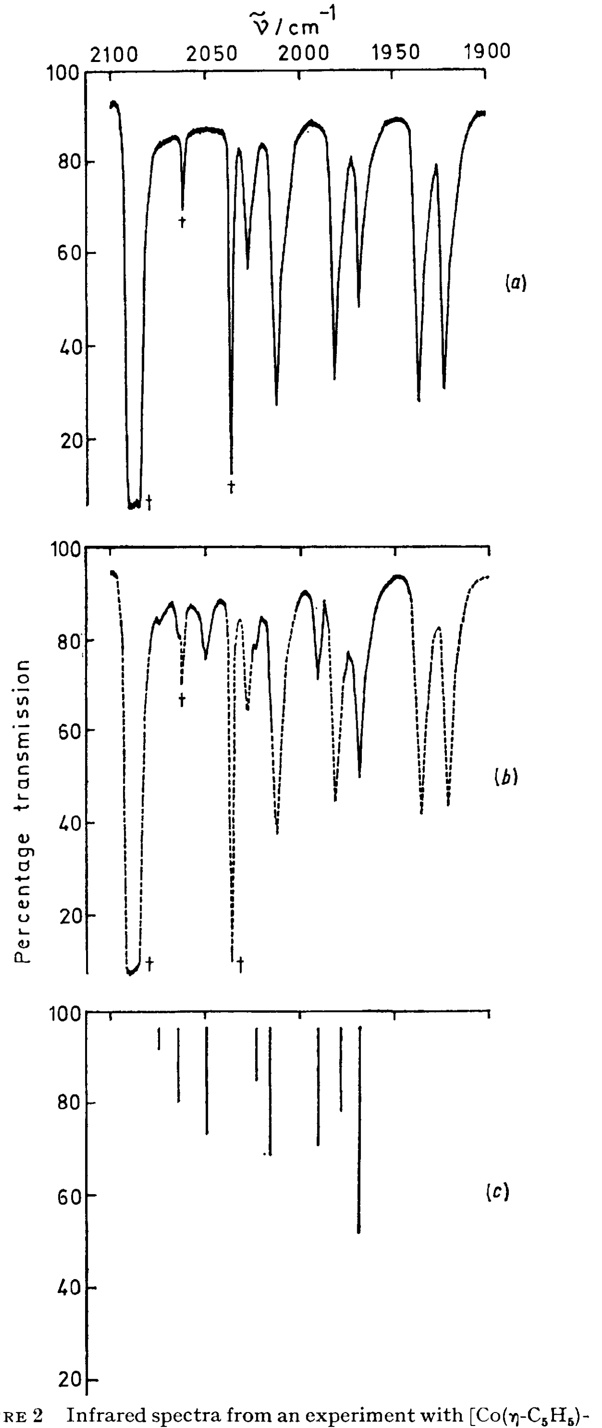

FIGURE 2 Infrared spectra from an experiment with [Co(η-C_5H_5)(CO)$_2$] isolated in a CO matrix with *ca.* 60% ^{13}CO enrichment: (*a*) after deposition, (*b*) after photolysis for 15 min with filter A, and (*c*) predicted spectrum for C_{3v} [Co(η-C_5H_5)(CO)$_3$] with *ca.* 60% enrichment. Bands marked † are due to CO isotopes in the host matrix and the other broken lines in (*b*) are due to the parent molecule bands which are not under consideration

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* The mean error was measured as $(\sigma^2/n)^{\frac{1}{2}}$.

calculate the band positions for all possible enriched molecules. There is an extremely good fit for observed and calculated band positions (Table 2; mean error = 0.32 cm^{-1}, maximum error = 0.8 cm^{-1}). However, conclusive proof is obtained by calculating the corresponding intensity pattern for each species and using this together with the relative abundance of each ^{13}CO-enriched species (for a total enrichment of *ca.* 60% distributed statistically) to construct a calculated spectrum [Figure 2(*c*)]. Comparison of the observed and calculated spectra [Figure 2(*b*) and 2(*c*)] confirms that the photoproduct contains the M(CO)$_3$ fragment with C_{3v} symmetry and a bond angle of 100.4 ± 1.0°.

TABLE 2

Observed and calculated [a] wavenumbers (cm^{-1}) of terminal CO-stretching bands in experiments with *ca.* 60% ^{13}CO-enriched [Co(η-C$_5$H$_5$)(CO)$_2$] isolated in a CO matrix and *ca.* 60% ^{13}CO-enriched [Co(η-C$_5$H$_5$)(CO)$_2$] isolated in a pure N$_2$ matrix

Complex	ν(CO)		Observed	Calculated
[Co(η-C$_5$H$_5$)(^{12}CO)$_2$]	C_{2v}	A_1	2 032.1	2 031.4
		B_1	1 971.9	1 971.4
[Co(η-C$_5$H$_5$)(^{12}CO)(^{13}CO)]	C_s	A'	2 016.7	2 016.2
		A''	1 941.5	1 942.0
[Co(η-C$_5$H$_5$)(^{13}CO)$_2$]	C_{2v}	A_1	1 985.5	1 986.2
		B_1	1 927.1	1 927.6
[Co(η^3-C$_5$H$_5$)(^{12}CO)$_3$]	C_{3v}	A_1	2 075.0	2 075.0
		E	2 018.0	2 018.0
[Co(η^3-C$_5$H$_5$)(^{12}CO)$_2$(^{13}CO)]	C_s	A'	2 065.8	2 065.6
		A'	2 018.0 [b]	2 018.0
		A''	1 983.0 [b]	1 982.2
[Co(η^3-C$_5$H$_5$)(^{12}CO)(^{13}CO)$_2$]	C_s	A'	2 053.0	2 053.4
		A''	1 994.0	1 993.9
		A'	1 973.2	1 973.2
[Co(η^3-C$_5$H$_5$)(^{13}CO)$_3$]	C_{3v}	A_1	2 028.6	2 028.9
		E	1 973.2	1 973.2
[Co(η-C$_5$H$_5$)(^{12}CO)(N$_2$)]	C_s	A'	1 981.1	1 980.3
[Co(η-C$_5$H$_5$)(^{13}CO)(N$_2$)]	C_s	A'	1 935.6	1 936.3

[a] For [Co(η-C$_5$H$_5$)(CO)$_2$] K = 1 618.6 and k_i = 48.5 N m^{-1}. For [Co(η^3-C$_5$H$_5$)(CO)$_3$] K = 1 676.7 and k_i = 31.4 N m^{-1}. For [Co(η-C$_5$H$_5$)(CO)(N$_2$)] K_{CO} = 1 584.5, K_{NN} = 1 932.3, and $k_{CO,NN}$ = 5.53 N m^{-1} and with ν(NN) at 2 164.6 cm^{-1} for both [Co(η-C$_5$H$_5$)(^{12}CO)(^{14}N$_2$)] and [Co(η-C$_5$H$_5$)(^{13}CO)(^{14}N$_2$)]. [b] Band obscured by overlap.

The similarity of the terminal CO-stretching band positions of the Co(CO)$_3$ product fragment (Table 1) to those of [Co(π-allyl)(CO)$_3$] [ν(CO) at 2 076 (A_1) and 2 025 (E) cm^{-1} in the gas phase] [17] suggests, by analogy, that the matrix photoproduct is [Co(η^3-C$_5$H$_5$)(CO)$_3$]. Such a structure is consistent with the lowering of the ring deformation mode (Table 1), which indicates a change in ring co-ordination, and avoids the need to propose a 20-electron configuration for the central cobalt atom. The existence of stable [M(η^3-C$_5$H$_5$)] complexes has recently been demonstrated by *X*-ray crystallography, *e.g.* [W(η^5-C$_5$H$_5$)(η^3-C$_5$H$_5$)(CO)$_2$].[18] A close examination of the crystal structure reveals that the η^3-C$_5$H$_5$ ligand is bent, with an angle of 20° between the allylic and olefinic systems, so as to remove part of the π system from the co-ordination sphere of the metal.[18]

Photolysis of [Co(η-C$_5$H$_5$)(CO)$_2$] *in* N$_2$ *Matrices*.—The i.r. spectrum of [Co(η-C$_5$H$_5$)(CO)$_2$], isolated in a pure N$_2$ matrix at a dilution of 1 : 2 000, in the terminal CO-stretching and ring-deformation regions is shown in Figure 3(*a*). The two terminal CO-stretching bands (2 034.7 and 1 974.6 cm^{-1}) correspond to the A_1 and B_1 modes and the relative intensity of the bands (0.94 for A_1 : B_1) gave a OC–M–CO angle of 91.8 ± 1.0°.

A period of u.v. photolysis, using the medium-pressure mercury arc and filter A, produced new i.r. bands [Figure 3(*b*)] at 2 164.6, 2 138.0, 1 981.1 and 806.3 cm^{-1}, of which the band at 2 138.0 cm^{-1} corresponds to CO liberated by photolysis. The bands at 2 164.6 and 1 981.1 cm^{-1} increased with a constant relative intensity during subsequent periods of photolysis and, taking into account the dilution, can be assigned to a single mononuclear species. The band at 2 164.6 cm^{-1} can be assigned to a ^{14}N–^{14}N stretching mode because, on using a mixed ^{14}N$_2$–^{15}N$_2$ matrix (3 : 1) a new band was observed on photolysis at 2 096.1 cm^{-1} in accordance with the change in reduced mass from ^{14}N$_2$ to ^{15}N$_2$ (Table 1). Thermal ^{13}CO enrichment of [Co(η-C$_5$H$_5$)(CO)$_2$] in the gas phase followed by experiments in ^{14}N$_2$ matrices showed the production of only one new band at 1 935.6 cm^{-1} and this led to the conclusion that the photoproduct was a monocarbonylmono(dinitrogen)cobalt species, [Co(η-C$_5$H$_5$)(CO)(N$_2$)]. This is in contrast to the low-temperature solution study where no dinitrogen-stretching bands were observed [5] although they had been anticipated.[19] Long-wavelength irradiation (filter B) failed to reverse the primary photoreaction and this is analogous to the behaviour of [Cr(η-C$_6$H$_6$)(CO)$_2$(N$_2$)] and [Mn(η-C$_5$H$_5$)(CO)$_2$(N$_2$)],[12] which both have ν(NN) in the 2 160 cm^{-1} region, and in

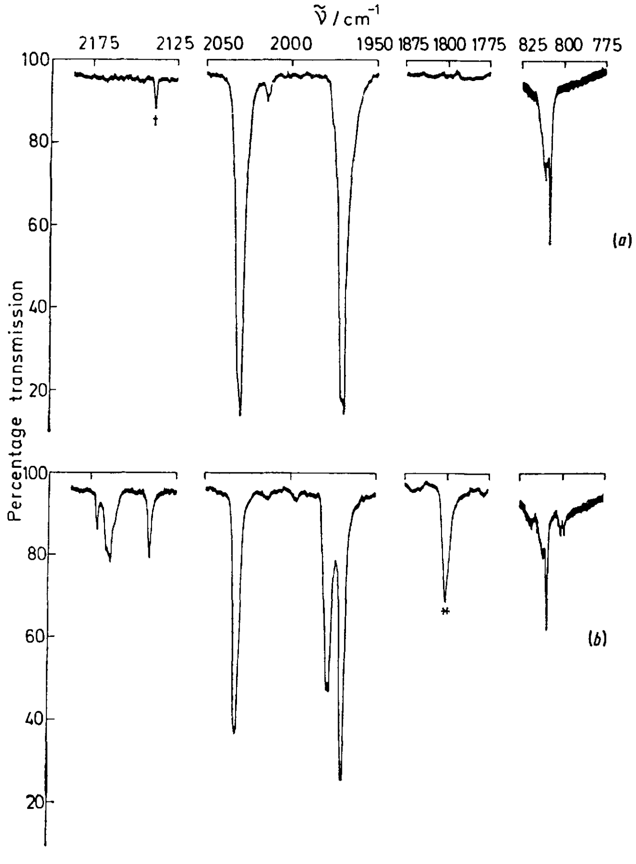


FIGURE 3 Infrared spectra from an experiment with [Co(η-C$_5$H$_5$)(CO)$_2$] isolated in a N$_2$ matrix: (*a*) after deposition and (*b*) after photolysis for 15 min with filter A. The band marked † in (*a*) is due to CO arising from slight decomposition and that marked * in (*b*) grows in only after further periods of annealing and photolysis (see text)

contrast to the behaviour of $[Fe(\eta\text{-}C_4H_4)(CO)_2(N_2)]$ [12] and other matrix-isolated dinitrogen complexes, *e.g.* $[Ni(CO)_3(N_2)]$,[20] which have $\nu(NN)$ above 2 200 cm^{-1}.

Annealing the matrix to 30 K, by switching off the Displex refrigerator and monitoring the temperature rise and then cooling the matrix back to 12 K by switching on the refrigerator, also failed to reverse the primary photoreaction although some changes occurred in the band-splitting patterns. However, on further photolysis (filter A) another band at 1 798.9 cm^{-1} began to grow in [band marked * in Figure 3(*b*)]. Subsequent cycles of annealing and photolysis caused this band to grow at the expense of the bands at 2 164.6 and 1 981.1 cm^{-1}. The facts (*i*) that the growth of the new band was accompanied by growth of no other NN- and CO-stretching bands, (*ii*) that the new band was shown to be a CO-stretching band by ^{13}CO-enrichment studies (Table 3), and (*iii*) that the band was also observed in analogous experiments in Ar and CH_4 matrices (see below) can be accounted for by the possibilities that the new band arises from $[Co(\eta\text{-}C_5H_5)(CO)]$ or $[\{Co(\eta\text{-}C_5H_5)(CO)\}_2]$ species. The former explanation seems unlikely because, by analogy with $[Mn(\eta\text{-}C_5H_5)(CO)_n]$ (n = 2 or 3),[12] the terminal CO-stretching band of $[Co(\eta\text{-}C_5H_5)(CO)]$ is predicted to occur at *ca.* 1 960 cm^{-1} (Table 4). The latter possibility, however, is consistent with the position of the antisymmetric bridging CO-stretching band of $[\{Co(\eta\text{-}C_5H_5)(CO)\}_2]$ (1 798 cm^{-1}, high-boiling light petroleum).[5] The presence of this species in the matrix is not improbable because annealing allows the matrix to soften so that two near neighbours can come together and on photolysis form a dimeric product. As expected, experiments with increased dilution (>1 : 5 000) did not show the formation of any appreciable amount of the species whereas at lower dilutions (*ca.* 1 : 1 000) its formation was enhanced. In analogous experiments with 50% ^{13}CO-enriched $[Co(\eta\text{-}C_5H_5)(CO)_2]$ new bands were observed at 1 813.9w, 1 798.9s, 1 766.5s, and 1 758.1s cm^{-1}. The three strong bands are analogous to the pattern for the antisymmetric bridging CO-stretching modes of ^{13}CO-enriched $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$ (1 857.2s, 1 826.0s, and 1 814.4s cm^{-1}). Comparison of the observed and calculated band positions for $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$ and the photoproduct (Table 3) confirms that the photoproduct is $[\{Co(\eta\text{-}C_5H_5)(CO)\}_2]$. The fact that the symmetric CO-stretching band for $[\{Co(\eta\text{-}C_5H_5)(CO)\}_2]$ (1 813.9w cm^{-1}) is only observable for the mono-^{13}CO-enriched species is consistent with the suggestion [5] that the $Co(\mu\text{-}CO)_2Co$ fragment is planar whereas for the $Ni(\mu\text{-}CO)_2Ni$ fragment which is non-planar [21] the symmetric stretching modes are of medium intensity.

TABLE 3

Observed [a] and calculated [b] wavenumbers (cm^{-1}) for isotopically ^{13}CO-enriched $[\{Co(\eta\text{-}C_5H_5)(CO)\}_2]$ and $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$ complexes (C_{2v} geometry) in the terminal CO-stretching region

Complex	ν(CO)		Observed	Calculated
$[Co_2(\eta\text{-}C_5H_5)_2(^{12}CO)_2]$	C_{2v}	A_1	*c*	1 821.2
		B_1	1 798.9	1 798.7
$[Co_2(\eta\text{-}C_5H_5)_2(^{12}CO)(^{13}CO)]$	C_s	A'	1 813.9	1 812.8
		A''	1 766.5	1 766.8
$[Co_2(\eta\text{-}C_5H_5)_2(^{13}CO)_2]$	C_{2v}	A_1	*c*	1 780.7
		B_1	1 758.1	1 758.6
$[Ni_2(\eta\text{-}C_5H_5)_2(^{12}CO)_2]$	C_{2v}	A_1	1 895.9	1 895.3
		B_1	1 857.2	1 856.4
$[Ni_2(\eta\text{-}C_5H_5)_2(^{12}CO)(^{13}CO)]$	C_s	A'	1 884.0	1 883.4
		A''	1 826.0	1 826.7
$[Ni_2(\eta\text{-}C_5H_5)_2(^{13}CO)_2]$	C_{2v}	A_1	1 852.6	1 853.2
		B_1	1 814.4	1 815.2

[a] N_2 matrix. [b] For $[\{Co(\eta\text{-}C_5H_5)(CO)\}_2]$ K = 1 323.5 and k_i = 16.5 N m^{-1}. For $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$ K = 1 422.0 and k_i = 30.3 N m^{-1}. [c] Band too weak to observe.

TABLE 4

Band positions (cm^{-1}) for $[M(\eta\text{-}C_5H_5)(CO)_m]$ and $[M(\eta\text{-}C_5H_5)(CO)_n(N_2)]$ complexes and corresponding CO-factored stretching (K) and interaction (k_i) force constants (N m^{-1})

		ν(CO)		Force constants	
Complex	Matrix	sym	antisym	K	k_i
$[Mn(\eta\text{-}C_5H_5)(CO)_3]$ [a]	Ar	2 032.6	1 951.0	1 580.5	43.8
$[Mn(\eta\text{-}C_5H_5)(CO)_2]$ [a]	Ar	1 972.0	1 903.2	1 518.0	53.9
$[Mn(\eta\text{-}C_5H_5)(CO)_2(N_2)]$ [a]	N_2	1 978.7	1 927.0	1 535.2	40.3
$[Co(\eta\text{-}C_5H_5)(CO)_3]$	CO	2 075.0	2 018.0	1 676.7	31.4
$[Co(\eta\text{-}C_5H_5)(CO)_2]$	Ar	2 032.8	1 971.0	1 619.5	50.0
$[Co(\eta\text{-}C_5H_5)(CO)(N_2)]$	N_2	1 981.1		1 584.5	
$[Co(\eta\text{-}C_5H_5)(CO)]$	Ar	*ca.* 1 957 [b]		*ca.* 1 547 [b]	

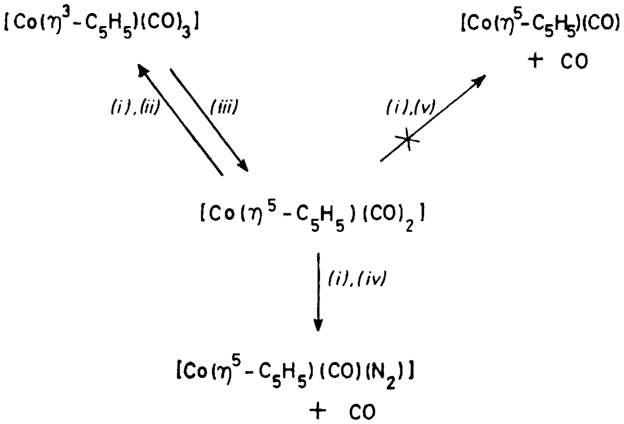
[a] Data from ref. 12. [b] Estimated band position and force constant.

In some experiments involving relatively concentrated matrices $\{[Co(\eta\text{-}C_5H_5)(CO)_2]:N_2$ = 1 : 1 000—2 000$\}$ a further weak band at 1 818.3 cm^{-1} was observed on initial photolysis with filter A. On further photolysis and annealing this band was replaced by the band at 1 798.9 cm^{-1} (see above). The band at 1 818.3 cm^{-1} may be tentatively assigned to the bridging CO-stretching mode of the monobridged dimeric species $[\{Co(\eta\text{-}C_5H_5)(CO)\}_2(\mu\text{-}CO)]$ on account of the dilution and by analogy with the band at 1 814 cm^{-1} observed for this species in high-boiling light petroleum,[5] the terminal CO-stretching bands being obscured by parent $[Co(\eta\text{-}C_5H_5)(CO)_2]$ bands {high-boiling light petroleum: ν(CO) (terminal) for $[Co(\eta\text{-}C_5H_5)(CO)_2]$ at 2 025 and 1 970 cm^{-1}, for $[\{Co(\eta\text{-}C_5H_5)(CO)\}_2(\mu\text{-}Co)]$ 1 965 cm^{-1}}.

Photolysis of $[Co(\eta\text{-}C_5H_5)(CO)_2]$ *in* Ar *and* CH_4 *Matrices.*— In contrast to other carbonylmetal and carbonylcyclopentadienylmetal complexes, *e.g.* $[Mn(\eta\text{-}C_5H_5)(CO)_3]$,[12] and carbonylnitrosylmetal and cyclopentadienylnitrosylmetal complexes, *e.g.* $[Mn(CO)_4(NO)]$ [22] and $[Ni(\eta\text{-}C_5H_5)(NO)]$,[23] photolysis of $[Co(\eta\text{-}C_5H_5)(CO)_2]$ in Ar and CH_4 matrices at high dilution led to *no* reduction in parent-band intensities and *no* new photoproduct bands. This was initially attributed to reverse photolysis occurring in the beam of the i.r. spectrometer and caused by visible radiation from the Nernst glowbar.[23] Use of a germanium disc filter to protect the sample while in the i.r. spectrometer beam (Ocli Optical Coatings Ltd.) and photolysis using the medium pressure mercury arc and filter A *in situ* in the sample compartment of the spectrometer while protecting the matrix sample with the Ge disc filter *both* failed to lead to the observation of new bands, as expected for $[Co(\eta\text{-}C_5H_5)(CO)]$. However, on reducing the dilution and performing cycles of annealing and photolysis, new bands were observed at 1 794.4 and 1 791.2 cm^{-1} for Ar and CH_4 matrices respectively (Table 1), which are analogous to the band at 1 798.9 cm^{-1} of [{Co(η-C_5H_5)(CO)}$_2$] in N_2 matrices. The failure to observe the [Co(η-C_5H_5)(CO)] species on photolysis of [Co(η-C_5H_5)(CO)$_2$] in Ar and CH_4 matrices at 12 K could be due to its ready rotation within the matrix cage,[21] *cf.* the rapid recombination of photolytically generated [Ni(CO)$_3$] with CO in Ar matrices at 30 K.[25, †]

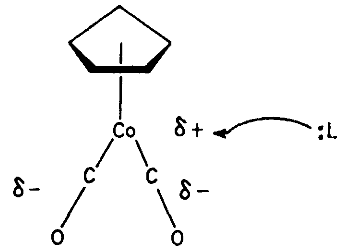
DISCUSSION

The photoreactions of [Co(η-C_5H_5)(CO)$_2$] at high dilutions in various matrices are shown in Scheme 1.



SCHEME 1 (*i*) *hν* (filter A), (*ii*) CO, (*iii*) *hν′* (filter B), (*iv*) N_2, and (*v*) Ar or CH_4

The observation of the expanded-co-ordination-number species, [Co(η^3-C_5H_5)(CO)$_3$], is consistent with the associative mechanism proposed[1,4] for substitution reactions of [Co(η-C_5H_5)(CO)$_2$]. A recent SCCMO calculation[26] has shown that there is a greater population in the carbonyl antibonding orbital for [Co(η-C_5H_5)(CO)$_2$], compared to other similar carbonylmetal complexes which undergo substitution by the dissociative mechanism, and that this relatively high π*-orbital population repulses the incoming nucleophile *towards* the more positive metal centre as shown in Scheme 2. In addition to electronic reasons for an associative reaction, steric considerations must also be important because [Co(η-C_5H_5)(CO)$_2$] is much more open to attack by an incoming nucleophile than other [M(η^5-C_5H_5)(CO)$_n$] complexes where $n \geqslant 3$. The value of the OC–Co–CO bond angle for [Co(η^3-C_5H_5)(CO)$_3$] (100°) is in good agreement with the OC–Co–CO bond angles for [Co(η^3-C_3H_5)(CO)$_3$] (two angles of 100.3° and one of 109.0°).[27]



SCHEME 2

The failure to observe [Co(η-C_5H_5)(CO)] on photolysis of [Co(η-C_5H_5)(CO)$_2$] at high dilution in Ar and CH_4 matrices suggests that there is probably an alternative explanation for the band which was previously[5] assigned to [Co(η-C_5H_5)(CO)]. On the basis of the photolysis of [Co(η-C_5H_5)(CO)$_2$] in N_2 matrices, the most likely candidate for the low-temperature solution photochemical reaction product is the complex [Co(η-C_5H_5)(CO)(N_2)]. Comparing the band positions in the N_2 matrix and high-boiling light petroleum for [Co(η-C_5H_5)(CO)$_2$] (2 034.7 and 1 974.6 *versus* 2 025 and 1 970 cm^{-1}) suggests that a solvent shift of 5—10 cm^{-1} should be subtracted from the N_2 matrix data for [Co(η-C_5H_5)(CO)(N_2)] to give the effective band positions for light petroleum solution. Applying this correction would give a predicted band in the range 1 971—1 976 cm^{-1} which correlates well with the band observed[5] for [Co(η-C_5H_5)(CO)] (1 970 cm^{-1}) whereas an equivalent correction applied to the estimated matrix band position for [Co(η-C_5H_5)(CO)] (*ca.* 1 957 cm^{-1}, Table 4) would predict a band at 1 947—1 952 cm^{-1} for light petroleum solution. Comparing the relative intensity and the half-width at half-height of the terminal NN- and CO-stretching bands for [Co(η-C_5H_5)(CO)(N_2)] (Figure 3) it is perhaps not surprising that in the low-temperature solution photochemical study a NN-stretching band was not observed.[5] On the basis of the matrix value for ν(NN) for [Co(η-C_5H_5)(CO)(N_2)] compared to values for [Mn(η-C_5H_5)(CO)$_2$(N_2)] and [Cr(η-C_6H_6)(CO)$_2$(N_2)] (2 164.6 *versus* 2 175.3 and 2 148.4 cm^{-1} respectively[12]) which are both stable crystalline complexes,[28,29] it is surprising that the photolysis product of [Co(η-C_5H_5)(CO)$_2$] in a low-temperature reaction swept with N_2 is [{Co(η-C_5H_5)(CO)}$_2$], although this result is analogous to the formation of [{Fe(η-C_4H_4)(CO)}$_2$(μ-CO)] on low-temperature photolysis of [Fe(η-C_4H_4)(CO)$_3$] in a tetrahydrofuran (thf) solution swept by N_2.[30] In this case, however, ν(NN) for matrix-isolated [Fe(η-C_4H_4)(CO)$_2$(N_2)] (2 206.8 cm^{-1})[12] is much closer to the value for free N_2 (2 331 cm^{-1}). Possibly a two-stage route, *cf.* [Cr(η-C_6Me_6)(CO)$_2$(N_2)][31] [equations (3) and (4)], would

$$[\mathrm{Cr}(\eta\text{-}C_6Me_6)(CO)_3] \xrightarrow[\text{thf}]{h\nu} [\mathrm{Cr}(\eta\text{-}C_6Me_6)(CO)_2(\text{thf})] + CO \quad (3)$$

$$[\mathrm{Cr}(\eta\text{-}C_6Me_6)(CO)_2(\text{thf})] + N_2 \xrightarrow{\text{thf}} [\mathrm{Cr}(\eta\text{-}C_6Me_6)(CO)_2(N_2)] \quad (4)$$

afford a successful synthesis of [Co(η-C_5H_5)(CO)(N_2)].

Conclusion.—The photoreaction of [Co(η-C_5H_5)(CO)$_2$] with CO in low-temperature matrices indicates that the reactive intermediate in solution substitution reactions is an expanded-co-ordination-number species involving electron transfer to the cyclopentadienyl ligand, *e.g.* [Co(η^3-C_5H_5)(CO)$_3$], in accordance with kinetic studies[1,4]

[†] Alternatively, following detection of a weak luminescence from [Co(η-C_5H_5)(CO)$_2$] in Ar and CH_4 matrices at 12 K (R. Narayanaswamy, A. J. Rest, and D. J. Taylor, unpublished work), failure to observe matrix photochemistry for [Co(η-C_5H_5)(CO)$_2$] may be due to efficient radiative and non-radiative decay processes for the excited-state species.

rather than a co-ordinatively unsaturated species formed by dissociation of a CO ligand, *i.e.* $[Co(\eta\text{-}C_5H_5)(CO)]$.[5] Furthermore, it seems possible that $[Co(\eta\text{-}C_5H_5)(CO)(N_2)]$ and also $[Co(\eta\text{-}C_5H_5)(CO)(RC{\equiv}CR)]$, which has been proposed[6] in the mechanism of polymerisation of alkynes by $[Co(\eta\text{-}C_5H_5)(CO)_2]$, are obtained as a result of *initial* formation of $[Co(\eta^3\text{-}C_5H_5)(CO)_2(N_2)]$ and $[Co(\eta^3\text{-}C_5H_5)(CO)_2(RC{\equiv}CR)]$.*

The *reversibility* of the photoreaction (5) is the *first*

$$[Co(\eta^5\text{-}C_5H_5)(CO)_2] + CO \rightleftharpoons [Co(\eta^3\text{-}C_5H_5)(CO)_3] \quad (5)$$

report of such behaviour and it considerably extends the scope of the matrix-isolation technique to investigations of intermediates in reactions which are proposed to proceed by an associative path in addition to its capability in respect of reactions which proceed by a dissociative path.[10]

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* Photolysis of $[Co(\eta\text{-}C_5H_5)(CO)_2]$ in Ar matrices containing 10% $CH_2{=}CH_2$ and $CH{\equiv}CH$ affords new bands at 1 979.7 and 1 989.8 cm^{-1} respectively which are preliminarily assigned[32] as the terminal CO-stretching bands of $[Co(\eta\text{-}C_5H_5)(CO)(CH_2{=}CH_2)]$ and $[Co(\eta\text{-}C_5H_5)(CO)(CH{\equiv}CH)]$ by analogy with $[Co(\eta\text{-}C_5H_5)(CO)(N_2)]$.

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