# The Photochemistry of Cyclopentadienyl Platinum Carbonyl Dimers: Characterization of $[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5R_5)_2]$ (R = H or Me) using Matrix Isolation and Fast Time-resolved Infrared Spectroscopy

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U.v. photolysis of $[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2]$, (**1a**), or $[\{Pt(CO)(\eta^5\text{-}C_5Me_5)\}_2]$, (**1b**), isolated in Ar, $N_2$, or CO matrices at 20 K causes ejection of a CO group and formation of $[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2]$, (**2a**), and $[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5Me_5)_2]$, (**2b**), respectively. Isotopic enrichment with $^{13}CO$ shows that these photoproducts contain only one bridging CO group. Photolysis using plane-polarised light demonstrates that this CO group occupies a position bridging the Pt–Pt bond symmetrically. Both (**2a**) and (**2b**) have strong absorptions in the visible region. Irradiation with light corresponding to these absorptions causes recombination with the photoejected CO to regenerate (**1a**) or (**1b**). The unsaturated species, (**2a**) and (**2b**), have also been identified at room temperature in solution, using time-resolved i.r. spectroscopy. They are found to have lifetimes in excess of 2 ms under these conditions, even in the presence of CO or $CH_3CN$. Prolonged u.v. photolysis also causes homolysis of the Pt–Pt bond of (**1a**) or (**1b**) in CO matrices, the resultant photoproduct being $[Pt(CO)_4]$.

Recently the photochemical reactions of dinuclear transition-metal cyclopentadienyl carbonyl compounds, both in solution and low-temperature matrices, have been the subject of extensive study.[1,2] The dimers $[\{M(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ (M = Cr, Mo, or W) and $[\{M(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ (M = Fe or Ru), have received particular attention.

It has been found that two primary photochemical processes occur in these complexes; (*i*) dissociative loss of CO to give a co-ordinatively unsaturated dinuclear complex, *e.g.* equation (1), and (*ii*) homolytic cleavage of the metal–metal bond to give mononuclear metal-centred radicals, *e.g.* equation (2). In low-

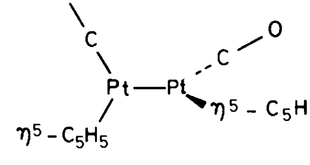
$$[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2] \longrightarrow [Fe_2(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_2] \quad (1)$$

$$[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2] \longrightarrow 2[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^{\bullet} \quad (2)$$

temperature matrices, however, ejection of a CO ligand is usually the sole observable process during the u.v. photolysis of these complexes.[3,4] Homolysis of the M–M bond is not observed, because the restrictions of the matrix cage lead to the instantaneous recombination of the bulky radicals. For both the iron and molybdenum complexes, flash photolysis[5,6] has demonstrated that the same dinuclear photoproducts are formed in room-temperature solution as in low-temperature matrices. Time-resolved i.r. spectroscopy[7] (a combination of u.v. flash photolysis and fast-i.r. detection) has recently proved a valuable tool in characterising these photoproducts in solution, since i.r. bands in the C–O stretching region provide more structural information than the broad featureless electronic absorption bands of these compounds.

The electronic structure of these dinuclear species is particularly intriguing. Sometimes multiple M–M bonds are formed, as in the case of the Group 6 metals, where photolysis in hydrocarbon solvents leads to the formation of the triply bonded dimers $[\{M(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ (M = Cr, Mo, or W) with very short M–M bond lengths.[8] The Fe dimer, $[Fe_2(\mu\text{-}CO)_3(\eta\text{-}C_5Me_5)_2]$, produced by photolysis of $[\{Fe(CO)_2(\eta\text{-}C_5Me_5)\}_2]$, is paramagnetic with a triplet ground state.[9,10]

Although the cyclopentadienyl complexes of nickel and platinum, $[\{M(CO)(\eta^5\text{-}C_5H_5)\}_2]$, were originally prepared by Fischer *et al.*[11] twenty five years ago, their photochemistry has been relatively neglected. The two compounds have markedly different structures. In the Ni complex, both CO groups bridge the metal–metal bond.[12] By contrast $[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2]$, (**1a**), and the recently synthesised complex $[\{Pt(CO)(\eta^5\text{-}C_5Me_5)\}_2]$, (**1b**), have two terminal CO groups,[13,14] with the relative orientation of the two Pt–CO bonds reminiscent of the two O–H bonds in $H_2O_2$.



(**1a**)

Preliminary investigations have shown that photolysis of $[\{Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)\}_2]$ in poly vinyl chloride matrices at 77 K causes dissociative loss of CO to form $[Ni_2(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2]$.[2] The analogous dinuclear Pt species, $[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2]$, (**2a**), with a single CO bridge has been proposed as an intermediate in the thermal reaction of (**1a**) with acetylenes, such as PhCCPh.[13] Matrix-isolation spectroscopy offers the possibility of characterising such a species.

In this paper we report the results of our investigation into the photochemistry of $[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2]$, (**1a**) and $[\{Pt(CO)(\eta^5\text{-}C_5Me_5)\}_2]$, (**1b**). Our experiments, in low-temperature matrices and in solution at room temperature (using time-resolved i.r. spectroscopy) have yielded detailed information about the structure of the intermediates, (**2a**) and (**2b**), formed on photolysis of these dimers.

## Experimental

The matrix isolation apparatus, Air Products Displex CS202, and photolysis equipment, Philips HPK 125-W medium

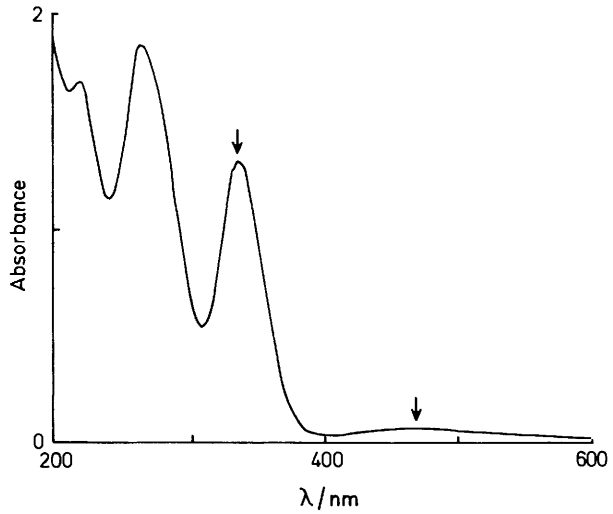


**Figure 1.** The electronic absorption spectrum of $[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2]$, (**1a**) ($10^{-4}$ mol dm$^{-3}$, 1-cm pathlength), in cyclohexane, at room temperature

pressure Hg arc, have been described previously.[15,16] Filters used for photolysis were a $NiSO_4$ (400 g dm$^{-3}$)–$CoSO_4$ (200 g dm$^{-3}$) aqueous solution (4-cm pathlength, band-pass, 230—345 nm) and a 290 nm (± 10 nm) Balzers interference filter. All i.r. spectra of matrix-isolated species were obtained using a Nicolet MX-3600 FT-IR interferometer and model 1280 data system (32 K data collect, 256 K Fourier transform, *i.e.* 0.7 cm$^{-1}$ resolution). U.v.–visible spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer with a model 3600 data station.

Matrices were prepared by 'slow spray-on' techniques,[16] with the sample of $[\{Pt(CO)(\eta^5\text{-}C_5R_5)\}_2]$ (R = H or Me) being heated to increase the rate of vaporisation. The concentration of sample in the matrix was varied both by changing the temperature used for vaporisation of $[\{Pt(CO)(\eta^5\text{-}C_5R_5)\}_2]$ and by altering the rate of deposition of the matrix gas. Temperatures used for sample vaporisation were typically 50 °C for $[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2]$ (**1a**) and 65 °C for $[\{Pt(CO)(\eta^5\text{-}C_5Me_5)\}_2]$ (**1b**). The results reported here were surprisingly insensitive to the initial concentration of $[\{Pt(CO)(\eta^5\text{-}C_5R_5)\}_2]$ in the matrix, even when the concentration was quite high, *ca.* 1:500. The temperature of the CsI matrix window was typically 17—20 K.

The principles and practice of polarised photochemistry have been described previously.[16,17,18] The experiments involve photolysing the matrix-isolated sample with plane-polarised light. I.r. and u.v.–visible spectra are recorded through a polariser with its plane of polarisation either parallel or perpendicular to the plane of the photolysing light. Comparison of the two spectra reveals whether absorption bands of the matrix-isolated species show any linear dichroism. The details of recording polarised i.r. spectra with the Nicolet MX-3600 have been given elsewhere.[16,18]

The time-resolved infrared spectroscopy apparatus [7,19] uses a pulsed-u.v. excimer laser (XeCl, 308 nm) as the u.v. photolysis source and a continuous wave CO i.r. laser, tunable in steps of 4 cm$^{-1}$ between 1 700 and 2 000 cm$^{-1}$, to monitor the absorption at a particular i.r. frequency. I.r. spectra are built up 'point by point' by repeating the u.v. flash photolysis with the i.r. monitoring laser tuned to a different wavenumber for each u.v. shot. As used here the time resolution of the apparatus was *ca.* 2 μs.

$[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2]$ (**1a**), $[\{Pt(CO)(\eta^5\text{-}C_5Me_5)\}_2]$ (**1b**) and $^{13}CO$-enriched $[\{Pt(CO)(\eta^5\text{-}C_5Me_5)\}_2]$ were prepared by standard literature methods.[13,14] Cyclohexane (BDH Aristar grade), matrix gases (Ar and $N_2$, Messer-Griesheim; CO, BOC research grade) were all used without further purification.

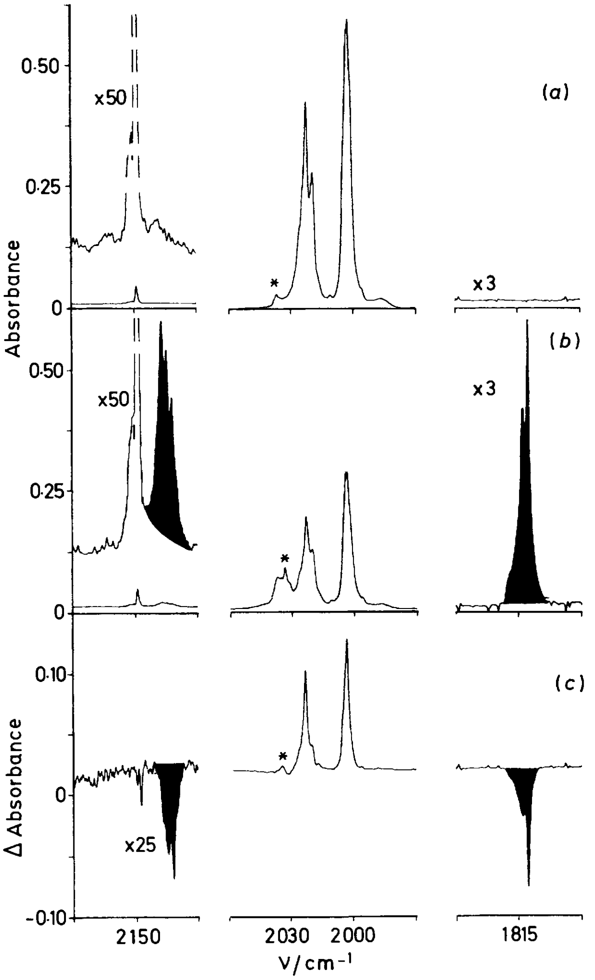


**Figure 2.** I.r. absorption spectra of $[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2]$, (**1a**). (*a*) After deposition in an argon matrix at 20 K; the band shown in broken lines is due to matrix-isolated molecular CO and the band marked * is due to an oligomeric species, formed by incomplete isolation of (**1a**). (*b*) After 90 min filtered u.v. irradiation (230—345 nm); filled-in bands are due to molecular CO and (**2a**) (see text). [The bands due to molecular CO observed on deposition, spectrum (*a*), have a slightly different wavenumber from that of the photoejected CO, spectrum (*b*). This is probably due to weak interactions with trace $H_2O$ impurities during deposition (H. Dubost and L. Abouaf-Marguin, *Chem. Phys. Lett.*, 1972, **17**, 269.)] (*c*) I.r. difference spectrum showing the effects of 90 min photolysis with visible light (>400 nm), *i.e.* spectrum before photolysis minus spectrum after. Negative peaks are due to CO and (**2a**) destroyed by the photolysis while positive peaks are due to the regeneration of (**1a**). Note the absorbance scale expansion factors in the different regions of the spectra

## Results and Discussion

*U.v. Photolysis of* $[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2]$, (**1a**).—The electronic absorption spectrum of $[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2]$, (**1a**), shown in Figure 1, is more structured than those of many related dinuclear transition-metal complexes. By analogy with previous studies on similar systems,[1,20] the two bands of lowest energy (arrowed) are assigned to the $d\pi\rightarrow\sigma^*$ and $\sigma\rightarrow\sigma^*$ transitions. It has also been suggested that the absorptions at higher energy are associated with transitions involving $M\rightarrow(CO)\pi^*$ charge transfer. Since the $\pi^*$ orbitals are M–C antibonding,[1,20] excitation of these charge-transfer transitions might be expected to lead to cleavage of an M–CO bond and formation of $[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2]$.

The i.r. spectrum of (**1a**) dissolved in hydrocarbon solvents at room temperature (not illustrated) is consistent with the *X*-ray structure, having two bands in the terminal ν(CO) region and none in the bridging ν(CO) region. The i.r. spectrum of (**1a**) isolated in an argon matrix at 20 K, Figure 2(*a*), is identical to the solution spectrum, apart from a small shift in wavenumber and a slight matrix splitting of one band. In the matrix spectrum, there is an additional weak band near 2 150 cm$^{-1}$ due to traces of unco-ordinated molecular CO in the matrix, probably originating from slight decomposition of $[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2]$ under vacuum. U.v. irradiation (230—345 nm) of the matrix leads to a decrease in intensity of i.r. bands of (**1a**) and the growth of two new absorptions* [filled-in bands in Figure 2(*b*)]. The lower wavenumber absorption is near 1 815 cm$^{-1}$, where bridging carbonyl groups normally absorb. The other new band, also filled in, is much less intense and is due to uncomplexed CO in the matrix. This suggests that u.v. photolysis is causing dissociative loss of CO from (**1a**) to form an unsaturated dinuclear intermediate, (**2a**), with a bridging CO group; see equation (3).

$$\underset{(\mathbf{1a})}{[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2]} \xrightarrow{\text{u.v.}} \underset{(\mathbf{2a})}{[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2]} + CO \quad (3)$$

During u.v. photolysis the matrix develops a striking pink colouration, easily visible to the naked eye after only a few minutes irradiation. The electronic absorption spectrum of the matrix after u.v. photolysis reveals a strong visible absorption with peaks at 470 and 522 nm not present before. These u.v.–visible bands grow in intensity at a rate, which exactly parallels the growth of the i.r. band due to the bridging CO group of (**2a**), see Figure 3. Thus it is reasonable to assume that the u.v.–visible bands are also associated with (**2a**).

Subsequent irradiation of the matrix with visible light (>400 nm), corresponding to excitation of these absorptions of (**2a**) causes the destruction of (**2a**) and regeneration of the starting material, (**1a**). This effect can be clearly seen from the i.r. difference spectrum shown in Figure 2(*c*). There are negative peaks, indicating a decrease in the amounts of both (**2a**) and molecular CO, and positive peaks showing the regeneration of (**1a**). The visible absorption bands of (**2a**) (470 and 522 nm) behave similarly to the bridging ν(CO) i.r. band (not illustrated). Thus, irradiation with visible light promotes the recombination of (**2a**) with CO, equation (4).

$$\underset{(\mathbf{2a})}{[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2]} + CO \xrightarrow{\text{visible}} \underset{(\mathbf{1a})}{[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2]} \quad (4)$$

Similar changes in the i.r. and u.v.–visible spectra are observed upon u.v. photolysis of the pentamethyl complex $[\{Pt(CO)(\eta^5\text{-}C_5Me_5)\}_2]$, (**1b**), isolated in an argon matrix at 20 K. A photoproduct, (**2b**), is formed with a bridging ν(CO) band at 1 772.0 cm$^{-1}$ and a visible absorption at 540 nm, again giving the matrix a bright pink colour. Excitation of (**2b**) with visible light again reverses the photochemical reaction, reforming (**1b**), albeit rather more slowly than in the case of the $C_5H_5$ compound. These results are in agreement with the photochemistry shown in equation (5). Formation of the same species,

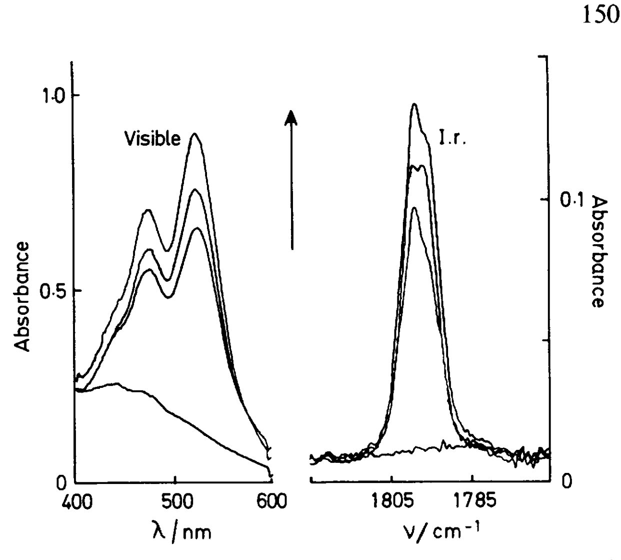


Figure 3. Visible and i.r. absorption bands showing the progressive formation of $[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2]$ (**2a**) after 0, 40, 80, and 120 min filtered u.v. photolysis of (**1a**), isolated in a CO matrix (the arrow indicates increasing photolysis time). U.v.–visible and i.r. spectra were recorded on the same sample. (Similar results were obtained for Ar and $N_2$ matrices.) Note that the relative intensities of the i.r. and visible bands remain constant, indicating that both absorptions belong to the same species, (**2a**)

$$\underset{(\mathbf{1b})}{[\{Pt(CO)(\eta^5\text{-}C_5Me_5)\}_2]} \underset{\text{visible}}{\overset{\text{u.v.}}{\rightleftharpoons}} \underset{(\mathbf{2b})}{[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5Me_5)_2]} + CO \quad (5)$$

(**2a**) and (**2b**), was observed in $N_2$ and CO matrices on photolysis of (**1a**) and (**1b**) respectively. The i.r. and u.v.–visible data for these experiments are summarised in Table 1.

*Identification of Intermediates.*—The results described in the previous section suggest that the most likely structures for (**2a**) and (**2b**) are $[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2]$ and $[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5Me_5)_2]$. Since these conclusions involve interpreting the relatively weak i.r. absorption due to photoejected CO, we now strengthen the case by using $^{13}CO$ isotopic enrichment to prove that (**2b**) contains only one CO group.

The photolysis experiments were repeated with samples 50% enriched with $^{13}CO$. If the photoproduct contained a single bridging CO group, one would expect two ν(CO) bands of almost equal intensity, corresponding to the $\mu\text{-}^{12}CO$ and $\mu\text{-}^{13}CO$ groups. If, however, the product contained two bridging CO groups, the arguments of Darling and Ogden[21] would predict four ν(CO) bands (3 strong, 1 weak) under these conditions.

Figure 4(*a*) shows the spectrum obtained after u.v. photolysis of (**1b**), with 50% $^{13}CO$ enrichment, isolated in an $N_2$ matrix at 20 K. Two ν(CO) bands of equal intensity are observed. These can be assigned to the two isotopomers of a photoproduct with one bridging CO group. The band at higher frequency, due to $[Pt_2(\mu\text{-}^{12}CO)(\eta^5\text{-}C_5Me_5)_2]$, has the same half-width, 8.5 cm$^{-1}$, as in experiments without isotopic enrichment, see Figure 4 (*b*). A doubly bridged structure, $[\{Pt(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)\}_2]$, could only give rise to the spectra in Figure 4 if the interaction force constant between the two CO groups were zero. This seems most improbable in view of the non-zero interaction constants found in related molecules such as $[\{Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)\}_2]$

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* There is also a broad band, marked with an asterisk, which grows in the terminal ν(CO) region during u.v. photolysis. This must be due to some oligomeric species, since it is much more prominent in experiments where the concentration of (**1a**) was deliberately high.

**Table 1.** Wavenumbers (cm$^{-1}$) of i.r. bands and wavelengths (nm) of u.v.–visible bands of (**1a**), (**1b**), and their photoproducts in different matrices at 20 K

| | Matrix gas | | | | | |
|---|---|---|---|---|---|---|
| | Ar | | $N_2$ | | CO | |
| Species | I.r. | U.v.–visible | I.r. | U.v.–visible | I.r. | U.v.–visible |
| (**1a**) $[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2]$ | 2 023.1* | | 2 017.0* | 260 | 2 015.2* | |
| | 2 003.1 | | 1 999.5* | 325 | 1 996.9 | |
| (**1b**) $[\{Pt(CO)(\eta^5\text{-}C_5Me_5)\}_2]$ | 1 992.8 | 290 | 1 992.1 | 290 | 1 987.8 | 295 |
| | 1 971.8* | 360 | 1 970.3 | 360 | 1 966.4 | 364 |
| (**2a**) $[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2]$ | 1 810.4* | 470 | 1 806.1 | 474 | 1 996.9* | 478 |
| | | 522 | | 525 | | 528 |
| (**2b**) $[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5Me_5)_2]$ | 1 772.0* | 540 | 1 770.0* | 540 | 1 759.6* | 545 |

* Average wavenumber of bands split by matrix effects.

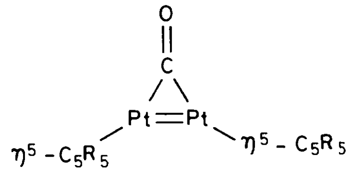
and $[(\eta^5\text{-}C_5H_5)(CO)Fe(\mu\text{-}CO)_2Ni(\eta^5\text{-}C_5H_5)]$.[12,22,23] The observed and calculated wavenumber data for these isotopic experiments are summarised in Table 2.

We have now established that u.v. photolysis of (**1a**) and (**1b**) generates monocarbonyl species (**2a**) and (**2b**) and have eliminated the possibility that the photoproducts contain two or more bridging CO groups, which give rise to only one ν(CO) absorption due to some geometrical quirk of the structure, *e.g.* a planar $[Pt_2(\mu\text{-}CO)_2]$ moiety. There are, however, a number of possible structures for (**2a**) and (**2b**), two of which (**A**) and (**B**) are illustrated. Structure (**A**) with a symmetrically bridging CO group contains the previously unknown (formal) Pt=Pt double bond, and could in principle be singlet or triplet; (**B**) possesses a semi-bridging CO group, potentially a four-electron donor. We now show how photolysis with plane-polarised light can eliminate structure (**B**).

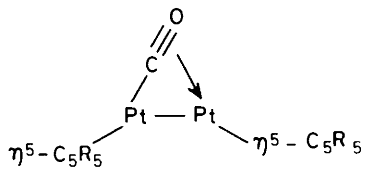
**Table 2.** Data for isotopic enrichment experiments; observed and calculated wavenumbers (cm$^{-1}$) of the ν(CO) bands for the isotopomers of (**1b**) and (**2b**) isolated in an $N_2$ matrix at 20 K

| Species | Observed | Calculated |
|---|---|---|
| (**1b**) $[Pt_2(^{12}CO)_2(\eta^5\text{-}C_5Me_5)_2]$ | 1 970.3 | 1 970.4[a] |
| | 1 992.1 | 1 991.6[a] |
| $[Pt_2(^{12}CO)(^{13}CO)(\eta^5\text{-}C_5Me_5)_2]$ | 1 930.8 | 1 930.8[a,b] |
| | 1 982.8 | 1 983.2[a,b] |
| $[Pt_2(^{13}CO)_2(\eta^5\text{-}C_5Me_5)_2]$ | 1 922.8 | 1 922.6[a,b] |
| | 1 943.2 | 1 943.4[a,b] |
| (**2b**) $[Pt_2(\mu\text{-}^{12}CO)(\eta^5\text{-}C_5Me_5)_2]$ | 1 770.0 | 1 770.0[c] |
| $[Pt_2(\mu\text{-}^{13}CO)(\eta^5\text{-}C_5Me_5)_2]$ | 1 727.6 | 1 730.6[c] |

[a] Calculated with the use of the C–O stretching force constant $k$ = 1 585.39 N m$^{-1}$, and interaction constant $k_i$ = 17.03 N m$^{-1}$. [b] To achieve the best fit the reduced mass of the $^{13}CO$ group was treated as a variable in these calculations. [c] Calculated with the use of the C–O stretching force constant $k$ = 1 265.6 N m$^{-1}$.



(**A**)



(**B**)

*Photolysis using Plane Polarised Light.*—This technique, briefly described in the Experimental section, has been valuable for studying the photochemistry of dinuclear metal carbonyls in low-temperature matrices.[18,24] Using this method, Dunkin *et al.*[24] were able to show that $[Mn_2(CO)_9]$ contained a semi-bridging CO group.

In our experiment, an $N_2$ matrix containing (**1b**) was photolysed with plane polarised light (290 nm) and i.r. and u.v. spectra were recorded with polarisers parallel and perpendicular to the plane of the photolysing light, see Figure 5. The analysis of these spectra involves two stages: (*i*) the linear dichroism in the bands of (**1b**) is used to establish that direction of the photoactive transition moment which lies along the axis of the Pt–Pt bond and (*ii*) given this orientation the presence of dichroism in the i.r. band of (**2b**) can be used to distinguish between a ketonic and a semi-bridging CO group; a ketonic-bridging CO group [as in (**A**)] should show linear dichroism while a semi-bridging CO group, lying at approximately 45° to the Pt–Pt bond [as in (**B**)] should not.*

We first consider the bands of those molecules of (**1b**) which remain intact after polarised photolysis. In such circumstances the photoactive u.v. absorption will always display dichroism perpendicular to the plane of polarisation of the photolysing light. By contrast, both i.r. bands of (**1b**) exhibit dichroism parallel to this plane [Figure 5(*a*)]. Thus, the directions of the transition moments of the ν(CO) modes and the photoactive u.v. transition must be orthogonal. Given the structure of (**1b**) (as already seen), the symmetric and antisymmetric ν(CO) modes have dipole moment changes in a plane, almost perpendicular to the axis of the Pt–Pt bond. The photoactive transition moment must therefore be parallel to the Pt–Pt bond.

The u.v. absorption of (**1b**) at 360 nm was also observed to be dichroic, as shown in Figure 5(*b*), such that its transition moment must be parallel to that of the photoactive transition (290 nm), *i.e.* lying along the Pt–Pt bond. This is consistent with

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* This argument assumes no rotation of the Pt–Pt bond within the matrix cage on ejection of CO, which is reasonable considering the size of the molecule.

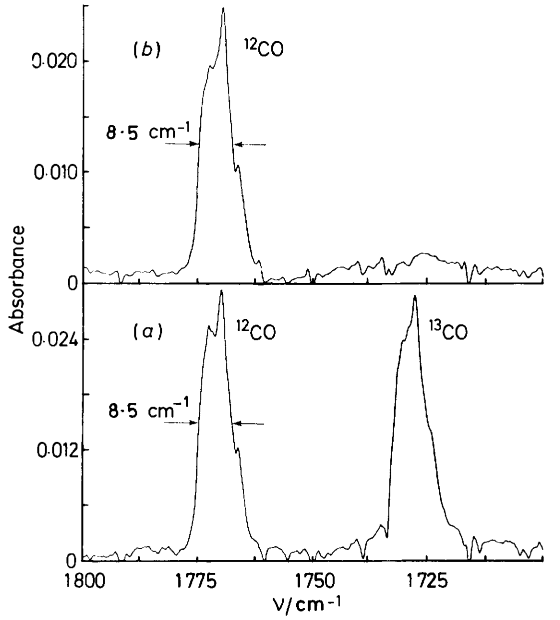

**Figure 4.** I.r. spectra showing how $^{13}$CO enrichment establishes the number of bridging CO groups in (**2b**). (*a*) The bands observed after 30 min filtered u.v. photolysis of (**1b**), 50% enriched with $^{13}$CO and isolated in a $N_2$ matrix. The two bands are assigned to $[Pt_2(\mu\text{-}^{12}CO)(\eta^5\text{-}C_5Me_5)_2]$ and $[Pt_2(\mu\text{-}^{13}CO)(\eta^5\text{-}C_5Me_5)_2]$. (*b*) The spectrum observed when an unenriched sample of (**1b**) was photolysed under similar conditions. Note that the bands due to $^{12}$CO have identical half-widths in both experiments

the assignment of the 360 nm band to a $d\pi \rightarrow \sigma^*$ or $\sigma \rightarrow \sigma^*$ transition. It is also clear from Figure 5(*a*) that the i.r. band due to the bridging CO group of (**2b**) shows significant dichroism in a direction perpendicular to the plane of the photolysing light. Such dichroism is inconsistent with a semi-bridging CO group and therefore (**B**) can be rejected as a possible structure for (**2b**). The visible absorption band of (**2b**) at 540 nm, Figure 5(*b*), also shows dichroism, but parallel to the plane of the photolysing light indicating that the electronic transition moment must lie along the Pt–Pt bond.

*The Electronic Ground State of* $[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)_2]$.—It is much more dificult to determine the details of structure (**A**). The isoelectronic species $[Fe_2(\mu\text{-}CO)_3(\eta^5\text{-}C_5Me_5)_2]$ is a triplet, but this is because, by symmetry, the highest occupied molecular orbital is a doubly degenerate $\pi^*$ orbital.[9] We have attempted to determine whether (**2a**) and (**2b**) are paramagnetic by magnetic circular dichroism (m.c.d.).* Unfortunately the results of experiments using the m.c.d. matrix apparatus[25,26] at the University of East Anglia have so far been inconclusive.

Both (**2a**) and (**2b**) are surprisingly unreactive towards reagents added to the matrix. Thus, exactly the same photochemistry occurs in $N_2$ matrices as in Ar matrices. There is no evidence for formation of any other products corresponding to the dinitrogen complexes, $[Re_2(CO)_9(N_2)]$, which are observed when $[Re_2(CO)_{10}]$ is photolysed in $N_2$ matrices.[27] Such behaviour would be consistent with (**2a**) and (**2b**) having triplet ground states, since reaction with $N_2$ and similar ligands would be formally spin-forbidden. This lack of reactivity in (**2a**) and (**2b**) persists up to room temperature.

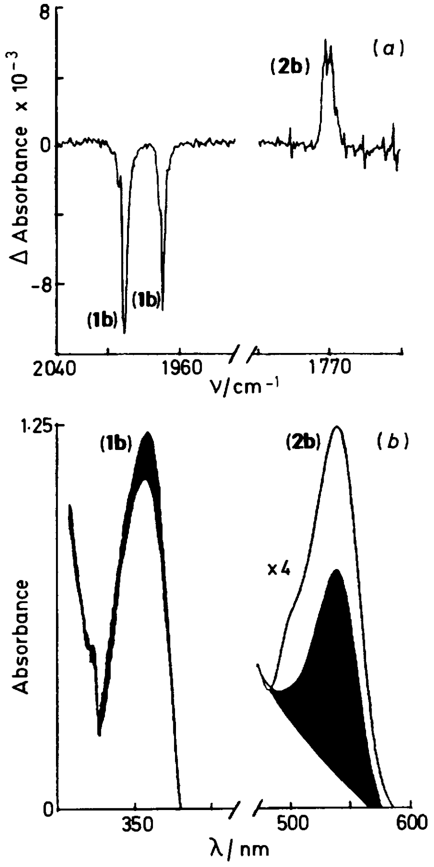

**Figure 5.** Spectra illustrating the dichroism generated by 60 h photolysis of (**1b**) in an $N_2$ matrix with plane-polarised light (290 nm). (*a*) I.r. difference spectrum ($A_\perp$ minus $A_\parallel$); bands are assigned to (**1b**) and (**2b**), as labelled. (*b*) Superimposed u.v.–visible spectra; the spectra recorded with the polariser perpendicular to the plane of photolysis, $A_\perp$, have been filled in to distinguish them from $A_\parallel$. U.v.–visible and i.r. spectra were recorded on the same sample

$[Pt_2(\mu\text{-}CO)(\eta^5\text{-}C_5Me_5)_2]$ *in Solution at Room Temperature*.—Time-resolved i.r. spectroscopy (t.r.i.r.) has already proved to be a successful method for detecting dinuclear intermediates in hydrocarbon solution at ambient temperatures.[7,19,28] U.v. flash photolysis of (**1b**) in cyclohexane solution generates an intermediate with a single i.r. absorption centred at 1 765 cm$^{-1}$, Figure 6. This wavenumber is very close to the absorption observed for (**2b**) in low-temperature matrices (see above) and can be reasonably assigned to the same species. The lifetime of (**2b**) in these room-temperature experiments was surprisingly long for an unsaturated species. The kinetic trace shown in the inset in Figure 6 illustrates that no significant decay of the i.r. absorption of (**2b**) was observable nearly 2 ms after the laser pulse. Similar traces were obtained even when CO or acetonitrile had been added to the solution, indicating that on this time-scale the lifetime of (**2b**) is unaffected by the presence of these potential reactants. T.r.i.r. experiments with (**1a**) revealed a transient species with an absorption at 1 802 cm$^{-1}$, very close to that of (**2a**) isolated in a matrix (see Table 1). (It was not feasible to heat the samples in these time-resolved experiments because of their thermal sensitivity in solution.) Experiments to determine more accurately the lifetimes of (**2a**) and (**2b**) in solution are in progress.

In all previous t.r.i.r. studies on dinuclear metal carbonyls,

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* Magnetic circular dichroism measurements on matrix isolated (**2b**) would appear to be an ideal method to determine its electronic ground state, since a paramagnetic species should exhibit a temperature-dependence in its m.c.d. spectrum, whereas that of a diamagnetic species should be independent of temperature.[26]

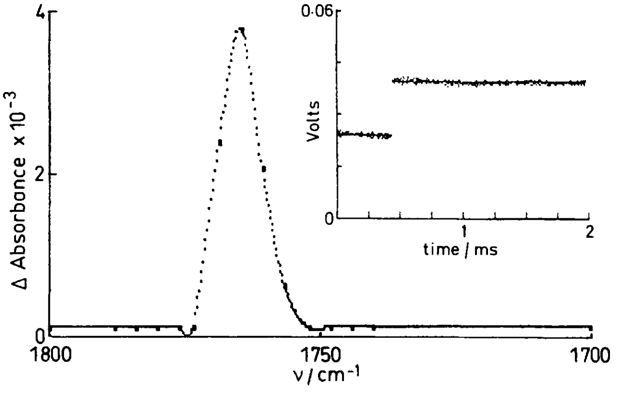

**Figure 6.** The transient i.r. absorption band observed 250 μs after u.v. laser flash photolysis of (**1b**) in cyclohexane solution at room temperature. (Experimental points are shown bold and lighter points are interpolated by computer.[19]) The inset illustrates the kinetic trace obtained at 1 764.7 cm$^{-1}$ showing no decay of the transient nearly 2 ms after the laser pulse

signals due to metal-centred free radicals, formed by homolysis of the M–M bond have been observed.[28] It was therefore surprising that we did not observe any signals attributable to [Pt(CO)($C_5R_5$)] radicals. Possibly the ν(CO) absorptions of [Pt(CO)($C_5R_5$)] lie outside the wavenumber range of our present t.r.i.r. spectrometer. However, kinetic traces due to the ν(CO) absorptions of (**1a**) and (**1b**) (not illustrated) showed no evidence for regeneration of the dimers from any other photoproducts such as radicals. It is possible that for photolysis at 308 nm, the quantum yield for bond homolysis is very much lower than that for CO loss. Under the conditions of our experiment, therefore, any signals due to [Pt(CO)($C_5R_5$)] may be too weak to be detected.

*Evidence for Photochemical Cleavage of the* Pt–Pt *Bond.*— Despite our t.r.i.r. results, there is considerable chemical evidence that homolysis of the Pt–Pt bond can occur. For example, u.v. photolysis of a mixture of (**1a**) and (**1b**) in hydrocarbon solution leads to the slow formation of a 'crossover' product,[29] equation (6). There is also evidence for

$$[\{Pt(CO)(\eta^5\text{-}C_5H_5)\}_2] + [\{Pt(CO)(\eta^5\text{-}C_5Me_5)\}_2] \xrightarrow{\text{u.v.}} 2[\{Pt(CO)(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)Pt(CO)\}] \quad (6)$$

bond homolysis in pure CO matrices, where chemical reaction with CO circumvents the problems of recombination within the matrix cage. Filtered u.v. irradiation (230—345 nm) of (**1a**) in a CO matrix produces results broadly similar to those observed in Ar matrices; the i.r. bands of (**1a**) decrease in intensity and the band of (**2a**) (filled in) grows in, see Figure 7(*a*) and (*b*). There are, however, two weak absorptions in the terminal C–O stretching region, arrowed in Figure 7(*b*), which are not observed in Ar matrices. There is a striking increase in the intensity of these arrowed bands after further photolysis of the matrix using unfiltered u.v.–visible light, Figure 7(*c*). The same bands are also observed, at exactly the same wavenumbers, when (**1b**) is photolysed with unfiltered u.v. light. This indicates that the photoproduct does not contain any $C_5R_5$ ligands since one would expect a significant shift in wavenumber between the species where R = H and R = Me. [There is a shift of *ca.* 30 cm$^{-1}$ between the ν(CO) bands in (**1a**) and (**1b**).] Thus the possibility of mononuclear species such as [Pt(CO)($\eta^5$-$C_5R_5$)], [Pt$(CO)_2$($\eta^3$-$C_5R_5$)], or [Pt$(CO)_3$($\sigma$-$C_5R_5$)] is eliminated.

However, the wavenumbers of the bands that we have observed, 2 054.0 and 2 047.6 cm$^{-1}$, correspond well with reported values for matrix-isolated [Pt$(CO)_4$], generated by co-condensation of Pt atoms and CO;[30] the bands are due to the $t_2$ ν(CO) stretching mode, split into two components by site effects in the solid CO matrix.

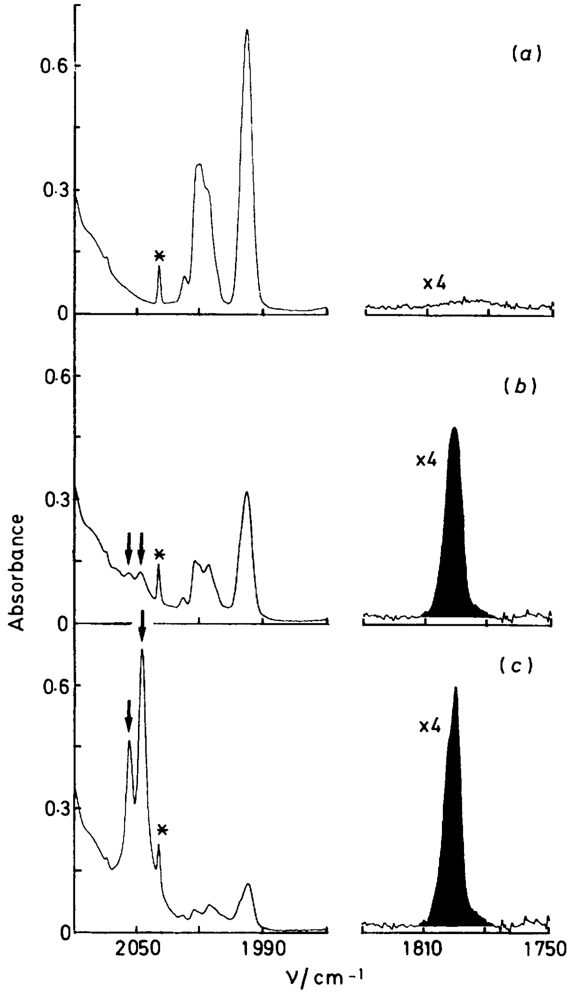

**Figure 7.** I.r. spectra illustrating the cleavage of the Pt–Pt bond in (**1a**). (*a*) After deposition of (**1a**) in a CO matrix at 20 K. The band marked * is due to a trace impurity of [Ni$(CO)_4$] in the CO matrix. (*b*) After 120 min filtered u.v. photolysis; the filled-in band is due to (**2a**). (*c*) After 90 min unfiltered u.v. photolysis; note the striking growth of the arrowed bands due to [Pt$(CO)_4$]

Under similar conditions [Pt$(CO)_4$] is generated more rapidly from (**1a**) than from (**1b**), indicating that the quantum yield for formation of [Pt$(CO)_4$] is larger for (**1a**) than for (**1b**). Although our experiments do not reveal the precise mechanism for the formation of [Pt$(CO)_4$], it is clear that photolysis can cause cleavage of the Pt–Pt bond in both (**1a**) and (**1b**).

## Conclusions

The results presented here have shown that photolysis of [{Pt(CO)($\eta^5$-$C_5H_5$)}$_2$] leads to loss of CO and formation of a relatively stable intermediate, [$Pt_2$($\mu$-CO)($\eta^5$-$C_5H_5$)$_2$], with a single bridging CO group. The fact that a CO group is bridging a bond between two third-row metal atoms makes an interesting contrast to [$Re_2(CO)_9$], which does not have any

CO bridges. The change from terminal to bridging CO groups is reminiscent of the photolysis of $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$[3,4] and such changes may transpire to be a characteristic feature of the photochemistry of cyclopentadienyl compounds. It is perhaps surprising that the quantum yield for homolysis of the Pt–Pt bond in **(1a)** and **(1b)** should be so low, particularly because formation of mononuclear species is common in these systems. Perhaps the higher quantum yield for loss of CO is partially offset by the low reactivity of the dinuclear intermediates. Tantalisingly, the electronic ground states of **(2a)** and **(2b)** remain unknown and it is hoped to carry out further experiments to try to resolve this question.

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