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Photochemistry of tris(dimethylpyrazolyl)-boratorhodium dicarbonyl and bis(dimethylpyrazolyl)-boratorhodium dicarbonyl complexes in low temperature media at 12–298 K: some insights into C–H activation processes

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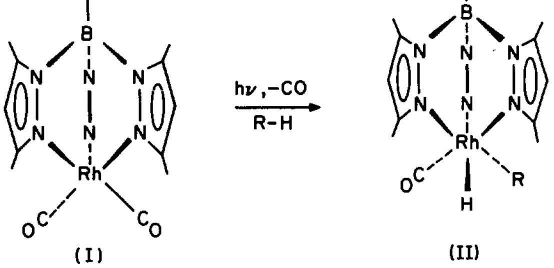
Abstract

IR and electronic spectroscopic evidence, including a study of ^{13}CO enrichment pathways, is presented to show that photolysis of tris(dimethylpyrazolyl)-boratorhodium dicarbonyl and bis(dimethylpyrazolyl)-boratorhodium dicarbonyl complexes in argon and methane matrices at *ca.* 12 K produces CO loss and ligand dechelation products. No evidence was found for photochemical C–H bond activation in methane matrices but the facile tridentate $\rightleftharpoons$ bidentate interconversion for tris(dimethylpyrazolyl)-boratorhodium dicarbonyl provides support for the proposal that such a process could be the key step in the highly efficient C–H photoactivation reaction of this complex at 298 K. In dinitrogen matrices the new CO loss products reacted to form monodinitrogen complexes. In an attempt to investigate whether additional thermal energy is needed for the photoactivation processes, the tris(dimethylpyrazolyl)-boratorhodium dicarbonyl and bis(dimethylpyrazolyl)-boratorhodium dicarbonyl complexes were photolysed in perfluorokerosine and Nujol mulls which could be warmed from *ca.* 12 K to 298 K. No C–H bond photoactivation was observed in Nujol mulls at 12 K or 77 K but at 298 K photoactivation of Nujol by tris(dimethylpyrazolyl)-boratorhodium dicarbonyl was observed, *i.e.* there appears to be a thermal contribution to the photochemical C–H activation process for this particular complex. The results of the low temperature studies are related to photochemical reactions observed in solutions at 298 K.

1. Introduction

Rapid advances have recently been made in developing organometallic complexes capable of activating alkane C–H bonds in homogeneous solutions [1]. Simultaneously, the use of the matrix isolation technique in combination with Fourier transform IR spectroscopy has enabled some species analogous to the intermediates proposed for C–H activation reactions to be observed [1–3]. Knowledge of the identity of such intermediates is crucial if more rational approaches are to be made to the understanding and harnessing of C–H activation process.

Pyrazolylborate–transition-metal chemistry has developed steadily over the past 20 years [4], but has only recently intersected the area of carbon–hydrogen activation when Ghosh and Graham reported [5] that the tris(dimethylpyrazolyl)-borato complex Rh(HB-Pz^*_3)-(CO)$_2$ (I, Pz* = 3,5-dimethylpyrazolyl) [6], photochemically activated aromatic and saturated hydrocarbons (eqn. (1)):



(I) (II) (1)

(IIa): R = C_6H_5
(IIb): R = Cyclohexyl
(IIc): R = CH_3

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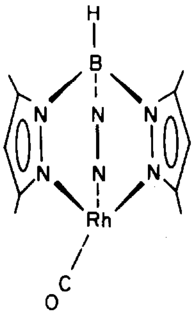
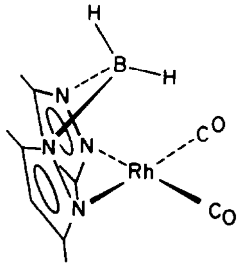
Ghosh and Graham found that when a benzene solution of **I** in a closed, evacuated Pyrex Schlenk tube was irradiated under their standard conditions [5] for 5 min, conversion to the hydridophenyl rhodium complex **IIa** according to eqn. (1) was complete. Under the same conditions, it had previously been found [7] that conversion of Ir(η^5-C_5Me_5)(CO)$_2$ to its corresponding hydridophenyl complex was only *ca.* 60% after 6 h irradiation and there was general decomposition if longer photolysis times were employed. Photoactivation reactions using Ir(η^5-C_5Me_5)(PMe$_3$)(H)$_2$ also required long irradiation times with powerful UV sources, and did not proceed to completion [8].

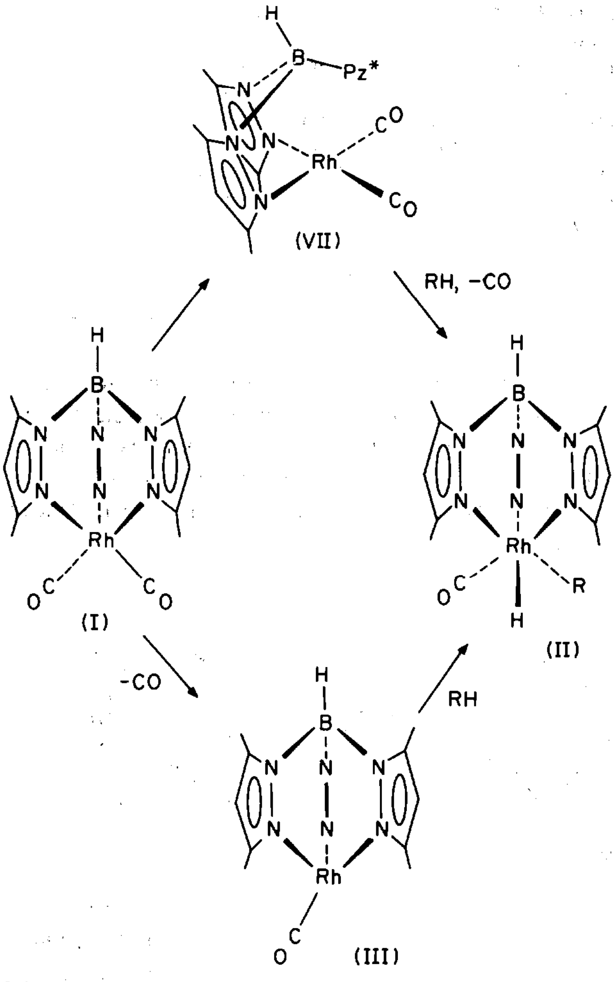
Ghosh and Graham [5] found that **I** was also capable of activating the C–H bonds of saturated hydrocarbons. If an N_2 or argon purge was used to prevent back reactions with released CO during photolysis, then irradiation of cyclohexane solutions of **I**, at room temperature, resulted in complete conversion to the cyclohexyl hydride **IIb** within 5 min. Changing the purge gas to CH_4 afforded both **IIb** and **IIc** as photoproducts. Photoactivation by **I** was also observed to proceed under daylight and laboratory (tungsten lamp) illumination as well as with the use of a mercury arc, so that it appears that photochemical C–H activation by **I** proceeds with high quantum efficiency.



(III)



(IV)



Scheme 1

On the basis of comparison with previous matrix studies [2,3] the most likely primary step in the photochemical C–H activation reaction would seem to be generation of the 16-electron species, Rh(HBPz$^*_3$)(CO) (**III**), formed by dissociative loss of CO. However, an alternative mechanism to initial CO loss might involve facile tridentate ⇌ bidentate interconversions of the tris(pyrazolyl) borate ligand as speculated by Graham and coworkers [5,9] (Scheme 1).

In order to try and understand the mechanism of C–H photoactivation, a matrix isolation study of the photochemistry of **I** and the related, stable 16-valence electron bis(dimethylpyrazolyl)borate complex Rh(H_2-BPz$^*_2$)(CO)$_2$ [10] (**IV**) in frozen gas matrices at *ca.* 12 K has been undertaken.

2. Experimental details

The equipment for low temperature studies, the spectrometers, the matrix gases, the techniques for using perfluorokerosine and Nujol mulls and paraffin waxes, and the photolysis lamp have been described previously [2,3]. (The formation of new species was monitored primarily using the terminal CO and NN stretching regions. Bands in the metal–nitrogen, ring deformation and B–H stretching regions were comparatively weak and did not show changes which could be correlated with structural changes in the species before and after photolysis).

Wavelength-selective photolysis was achieved:

Filter A

$\lambda < 280$ nm and $\lambda > 550$ nm

Quartz gas cell (pathlength 27 mm) containing Cl_2

gas (2 atm) + quartz gas cell (pathlength 27 mm) containing Br_2 gas (200 Torr)

Filter B
$290 < \lambda < 370$ nm and $\lambda > 550$ nm
Quartz gas cell (pathlength 27 mm) containing Br_2 gas (200 Torr) + Pyrex disc (thickness 2 mm)

Filter C
$330 < \lambda < 390$ nm
Corning glass filter No. 5874 (thickness 3 mm)

Filter D
$\lambda > 370$ nm
Corning glass filter No. 3060 (thickness 3 mm)

Filter E
$\lambda > 290$ nm
Pyrex disc (thickness 2 mm)

The complexes **I** and **IV** were kindly supplied by Professor W.A.G. Graham. Matrices containing the complexes were prepared by the slow spray-on method [11] since the complexes were insufficiently volatile to make up gas mixtures. The spray-on temperatures for **I** and **IV** were 75°C and 145°C respectively, *i.e.* well below the decomposition temperatures of the complexes, for example **I** decomposes to give $(HBPz^*_3)(Pz^*)_2Rh_2(CO)_2(H)$ at 217–223°C [4].

3. Results

Photolyses of the complexes studied in this paper were generally carried out with radiation similar in energy to that used in solution photochemical studies of **I** [5] and **IV** [12]. These correspond to the lowest energy electronic absorption bands of the complexes. Subsequently, higher energy photolyses were carried out with appropriate filters corresponding to higher energy UV absorptions (Table 1).

3.1. Photolysis of $Rh(H_2BPz^*_2)(CO)_2$ (IV) and $Rh(HBPz^*_3)(CO)_2$ (I) in argon and CH_4 matrices

The IR spectrum (terminal CO-stretching region) of **IV** isolated at high dilution in a pure argon matrix is shown in Fig. 1(a). The spectrum shows two strong terminal CO-stretching bands with weaker "satellite" bands, and is typical of dicarbonyl spectra of complexes of this type. The two strong bands correspond to the symmetric (A_1) CO-stretching mode (ν(CO) at 2084.0 cm^{-1}) and antisymmetric (B_1) CO-stretching mode (ν(CO) at 2018.2 cm^{-1}) of a dicarbonyl possessing C_{2v} local symmetry. The "satellite" bands (marked*) correspond to the CO-stretching modes of $Rh(H_2BPz^*_2)(^{12}CO)(^{13}CO)$ present in natural abundance.

TABLE 1. Electronic absorption bands for **I**, **IV** [a] and $Rh(acac)(CO)_2$ [a,b] complexes at high dilution in argon matrices [c] at *ca.* 12 K and *n*-hexane solution at room temperature

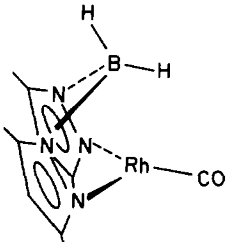
Complex	Medium	λ_{max}(nm) [d] (ϵ [e])	
		After deposition	After irradiation
I	Ar matrix	218(s)	–
		349(m)	–
	n-hexane	221(17600)	–
		353(1820)	–
IV	Ar matrix	225(s)	–
		280(s)	415(w)
		355(m)	
	n-hexane	228(14200)	–
		286(17800)	–
		358(2250)	–
$Rh(acac)(CO)_2$	Ar matrix	255(s)	–
		295(m)	400(w)
		304(sh)	
	n-hexane	285(s)	
		301(m)	
		323(sh)	

[a] Data also shown for the spectrum after irradiation showing broad bands for which the maxima were not easy to determine. Except for the possibility that these bands could be assigned to the monocarbonyl formed, they might be due to matrix effects. [b] Data from ref. 13 included for comparison. [c] Spectra in argon matrices are qualitative, since the quantity of sample deposited onto the cryostat window varied from experiment to experiment. Peaks at wavelengths shorter than 215 nm are overlapped by background scatter from some matrices. [d] s strong, m medium, w weak, sh shoulder. [e] Extinction coefficients only shown for solution data in this work.

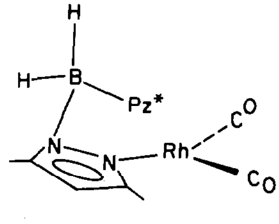
Short periods of photolysis (filter D) corresponding to the lowest energy electronic absorption band of **IV** (Fig. 2(a)), resulted in the production of "free" CO (*ca.* 2138 cm^{-1}) and a single new terminal CO-stretching band at 2002.4 cm^{-1}, together with a very weak new visible band. These new bands were produced at the expense of the IR and electronic absorption bands of the parent species (Figs. 1(b) and 2(b)). Photolysis with higher energy light (filter B) afforded a further two new IR bands, of similar intensities, at 2097.8 and 2024.1 cm^{-1}, along with further increases in the other new bands at 2002.4 cm^{-1} and 2138 cm^{-1} ("free" CO), all at the continued expense of the parent IR bands (Fig. 1(c)). Further even higher energy photolyses (filter A) resulted in an increase in all new IR bands, with the pair of new bands at 2097.8 and 2024.1 cm^{-1} appearing to grow together, while the band at 2002.4 cm^{-1} grew separately, becoming fairly intense (Fig. 1(d)). A final period of long wavelength irradiation (filter E), corresponding to the new weak visible electronic absorption band (Fig. 2(b)), saw the regeneration of the IR bands for **IV** at the expense of the new band at 2002.4 cm^{-1} and the band due to "free" CO, while the intensities of the other pair of new bands appeared to remain unchanged (Figs. 1(e) and 1(f)).

It is apparent that low energy photolysis of **IV** produced one product with an IR active band at 2002.4 cm^{-1} and a weak visible electronic absorption (λ_{max} = 415 mn, Table 1), whilst higher energy photolysis not only continued to produce this species, but also produced small amounts of further species (ν(CO) at 2097.8 and 2024.1 cm^{-1}). The corresponding production of "free" CO with the growth of the single IR band at 2002.4 cm^{-1} suggests this species is a product of photochemical CO loss from **IV**. Bearing in mind that the high dilution used in the experiments minimizes any polynuclear aggregation, it seems possible that this species is the monocarbonyl $Rh(H_2BPz_2^*)(CO)$ (**V**). A comparison of the terminal CO-stretching band positions in argon matrices for this proposed monocarbonyl *vs.* those for **IV** in comparison with the bands for $Rh(\eta^5\text{-}C_5H_5)(CO)$ (ν(CO) at 1968.5 cm^{-1}) [3] *vs.* $Rh(\eta^5\text{-}C_5H_5)(CO)_2$ (ν(CO) at 2053.0 and 1988.8 cm^{-1} [3], and for Rh(acac)(CO) (acac = acetylacetonate, ν(CO) at 2002.9 cm^{-1}) [13] *vs.* $Rh(acac)(CO)_2$ (ν(CO) at 2086.0 and 2109.5 cm^{-1}) [13] supports the assignment of this species as the monocarbonyl **V** (Table 2). Further support is provided by the observed photochemical reversal to **IV** on photolysis into the new low energy electronic absorption proposed to be due to **V**, and by results in N_2 and ^{13}CO doped matrices (see below and Table 3).

The other two new weak IR bands at 2097.8 and 2024.1 cm^{-1} are more difficult to assign. They both grow together on high energy photolysis of **IV** and then behave similarly on further photolyses and thus, as has been assumed, are likely to be due to a single species. This species must have a reduced electron density on the rhodium centre compared with that of the parent species **IV**, as the CO-stretching modes are at higher wavenumbers than those of the parent species. As there are two IR active carbonyl stretches which are apparently not related to the "free" CO band, it seems reasonable to suggest that the $Rh(CO)_2$ fragment of the parent species is retained in this unassigned photoproduct. A possibility, that would fit the above criteria, is the product of a facile bidentate to unidentate photoconversion of the pyrazolylborate ligand to form $Rh(\kappa^1\text{-}H_2BPz_2^*)(CO)_2$ (**VI**) (see Discussion).



(V)



(VI)

The IR spectrum (terminal CO-stretching region) of $Rh(HBPz_3^*)(CO)_2$ (**I**) isolated at high dilution in a pure argon matrix is shown in Fig. 3(a). This shows the expected two fairly strong terminal CO-stretching bands with weaker "satellite" bands due to $Rh(HBPz_3^*)(^{12}CO)(^{13}CO)$ present in natural abundance. (The bands observed were not as intense as those seen for **IV** in argon matrices, however, prolonged deposition or increasing deposition temperature only resulted in decomposition of the complex.)

Periods of photolysis (filter D) resulted in the production of a pair of new IR bands of similar intensities at 2086.1 and 2017.9 cm^{-1}, a very weak band centred at *ca.* 1966 cm^{-1} and a small trace of "free" CO (2138.2 cm^{-1}), whilst the parent bands decreased (Figs.

TABLE 2. Observed positions (cm^{-1}) of terminal CO-stretching modes of **I** and **IV** and their photoproducts in argon, CH_4, CO and N_2 matrices at *ca.* 12 K, mulls and waxes at 12–77 K and organic solvents at 298 K

Compound	Ar	CH_4	CO	N_2	PFK mull	Nujol mull [a]	Paraffin wax	Solution
I	2056.1	2055.2	2057.4	2058.3	2054	2054	2055	2054 [b]
	1985.2	1984.0	1985.7	1982.9	1981	1981	1974	1982
III	≈ 1966 [c]	≈ 1968 [c]	– [d]	– [d]	1961	1962	–	–
VII	2086.1	2086.3	≈ 2085 [e]	2088.2				2080 [b]
	2017.9	2019.4	2018.6	2020.2				2011
IV	2084.0	2085.2	2086.0	2087.1				2079.9 [f]
	2018.2	2016.0	2021.2	2022.0				2014.7
V	2002.4	2003.4	– [d]	2003.2			–	–
VI	2097.8	2100.2	– [d]	2105.3			–	–
	2024.1	2022.8		≈ 2027 [g]			–	–
VIII	–	–	–	2026.7 [h]	–	–	–	–
IX					2033 [j]	2037/2029 [k]		

[a] Unassigned product band at 298 K at 2006 cm^{-1} (see text). [b] Dichloromethane solvent from ref. 12. [c] Approximate position of a weak broad band. [d] Not detected. [e] Approximate position of a shoulder band to a strong host matrix band. [f] *n*-hexane solvent. [g] Approximate position of band superimposed on ν(CO) band of **VIII**, also present in the matrix. [h] ν(NN) at 2243.0 cm^{-1}. [j] See text. [k] 2037 cm^{-1} at 77 K and 2037 and 2029 cm^{-1} at 298 K.

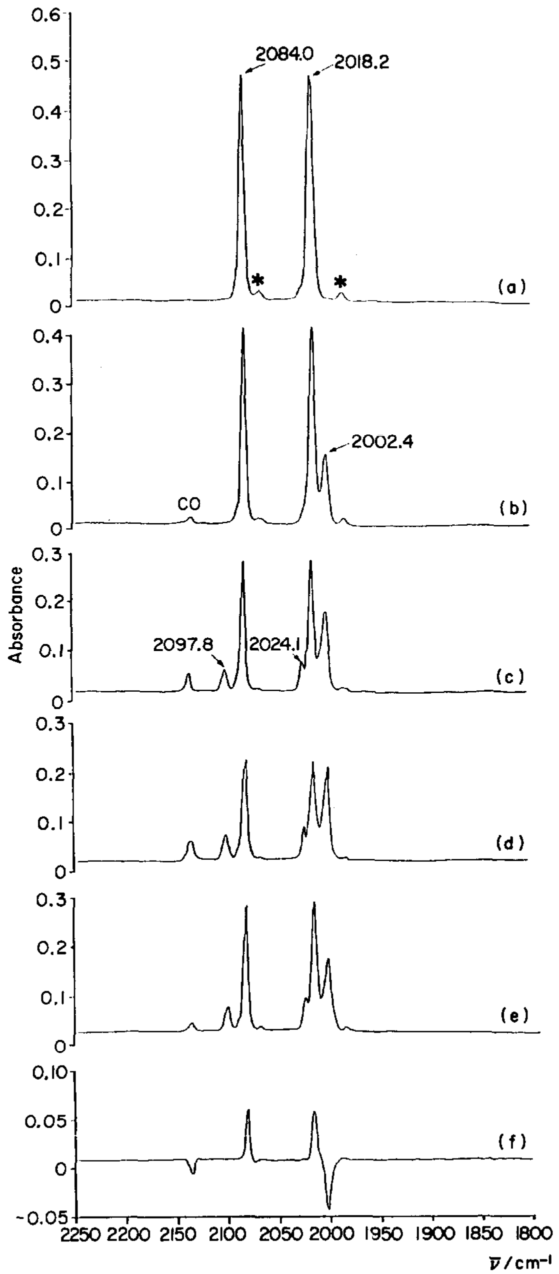


Fig. 1. IR spectra (Nicolet 7199 FTIR, 1 cm^{-1} resolution) from an experiment with IV isolated at high dilution in an argon matrix: (a) after deposition, (b) after 30 min irradiation (filter D); (c) after 20 min irradiation (filter B), (d) after 10 min irradiation (filter A), (e) after 2 h irradiation (filter E), and (f) subtraction spectrum ((e)-*A*(d)) where *A* is a scaling factor. Bands marked * arise from $Rh(H_2BPz_2^*)(^{12}CO)(^{13}CO)$ present in natural abundance.

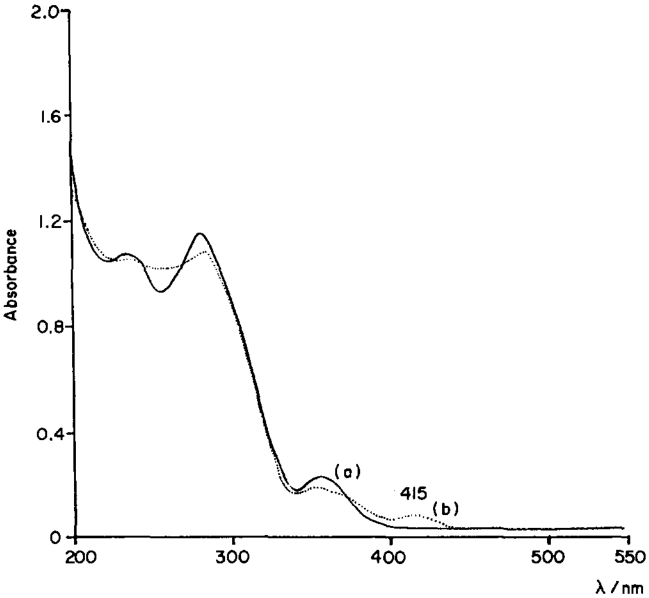


Fig. 2. Electronic absorption spectra (Perkin Elmer Lambda 7) of IV isolated at high dilution in an argon matrix: (a) after deposition and (b) after 30 min irradiation (filter D).

3(b) and 3(c)). Further higher energy photolyses with a variety of filters (filters H, B or A) failed to yield any other major changes in the IR spectrum apart from the slow growth of the two new bands at 2086.1 and 2017.9 cm^{-1}. On longer wavelength photolysis (filter E) the very weak band at *ca.* 1966 cm^{-1} and that for "free" CO were seen to disappear, but owing to their very weak intensities even computer subtraction facilities were unable to show a comparative growth in the parent IR bands. The low energy photolysis had no effect on the other pair of new bands. No clear changes in the electronic absorption spectrum of **I** were observed during photolysis.

The very weak band at *ca.* 1966 cm^{-1} can be assigned, *cf.* **V**, to the photoinduced CO loss product $Rh(HBPz_3^*)(CO)$ (**III**). However, only a very small amount of this species is produced, in contrast with **V**

TABLE 3. Observed and calculated positions (cm^{-1}) of terminal CO-stretching modes of IV and its photoproducts in 10% ^{13}CO doped CH_4 matrices

Compound	10% $^{13}CO/CH_4$ matrices	Calculated
$Rh(H_2BPz_2^*)(^{12}CO)_2$	2085.8 [a]	2085.4 [b]
	2016.3	2015.2 [b]
$Rh(H_2BPz_2^*)(^{12}CO)(^{13}CO)$	2068.7	2069.0 [b]
	1989.3	1989.0 [b]
$Rh(H_2BPz_2^*)(^{13}CO)_2$	2040.0 [c]	2039.1 [b]
	1970.3	1970.4 [b]
$Rh(H_2BPz_2^*)(^{12}CO)$	2002.9	–
$Rh(H_2BPz_2^*)(^{13}CO)$	1956.7	1958.3 [d]

[a] Shoulder band to host matrix ($^{13}C^{16}O$) band. [b] Calculated using refined stretching parameters ($K = 1698.9$ N m^{-1} and $k_i = 55.6$ N m^{-1}) obtained from the CO-stretching frequencies of $Rh(H_2BPz_2^*)(^{12}CO)_2$ and $Rh(H_2BPz_2^*)(^{12}CO)(^{13}CO)$ in 10% ^{13}CO doped CH_4. [c] Band obscured by host matrix ($^{13}C^{18}O$) band. [d] Calculated from the CO-stretching frequency of $Rh(H_2BPz_2^*)(^{12}CO)$ in 10% ^{13}CO doped CH_4, assuming no coupling of the CO vibration with other molecular vibrations.

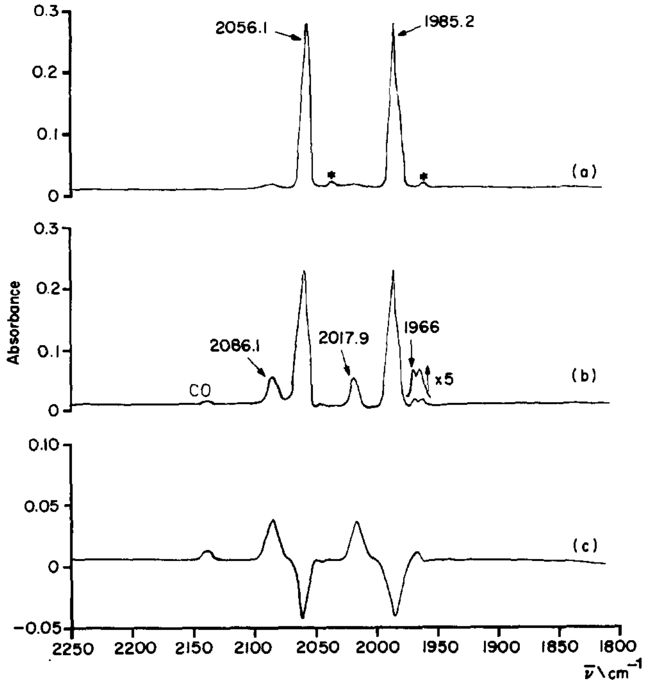
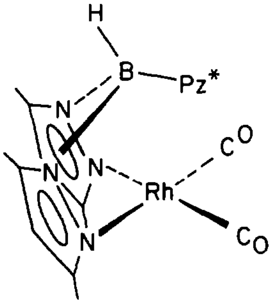


Fig. 3. IR spectra (Nicolet 7199 FTIR, 1 cm^{-1} resolution) from an experiment with **I** isolated at high dilution in an argon matrix: (a) after deposition, (b) after 50 min irradiation (filter D), and (c) subtraction spectrum ((b) − *B*(a)) where *B* is a scaling factor. Bands marked * arise from $Rh(HBPz_3^*)(^{12}CO)(^{13}CO)$ present in natural abundance.

which was the major product of photolysis of **IV**. A second species (ν(CO) at 2086.1 and 2017.9 cm^{-1}) was also produced on low energy photolysis in a much greater quantity. This species is apparently fairly stable and photochemically unreactive as it does not appear to undergo any further photochemistry after its production and no evidence was found for its reversal to **I**. The two bands are at higher wavenumbers than those of the parent and so the electron density on the rhodium centre of the new species must be reduced compared with the parent **I**, whilst the $Rh(CO)_2$ fragment appears to have been retained. A tridentate to bidentate conversion of the pyrazolylborate ligand to produce $Rh(\kappa^2\text{-}HBPz_3^*)(CO)_2$ (**VII**) would be consistent with the increase in ν(CO) as loss of the electron pair donation of the nitrogen atom of the "labile" pyrazolyl ring would reduce the electron density on the rhodium. A suitable model compound for **VII** (ν(CO) at 2086.1 and 2017.9 cm^{-1}) is the stable 16-electron species **IV** (ν(CO) at 2084.0 and 2018.2 cm^{-1}, Table 2). Allowing for slight shifts due to the proximity of the "labile" pyrazolyl ring the agreement is very good. The increase in ν(CO) in going from **I** to **VII** is consistent with the increase in ν(CO) observed for other metal carbonyl intermediates produced by photochemical loss of N-donor ligands and trapped in argon matrices, compared with their corresponding parent species [14]. For example, the complex $W(CO)_5$(pyridine) isolated in an argon matrix [14c] has CO-stretching modes centred at 2076.8, 1939.9 and 1926.9 cm^{-1} and on low energy photolysis $W(CO)_5$ (ν(CO) at 2097.3, 1962.8 and 1930.7 cm^{-1}) [14a] was produced. On the basis of these arguments the assignment of the bands at 2086.1 and 2017.9 cm^{-1} as due to the species **VII** seems reasonable (Table 2).

The assignment of **VII** also lends support to the assignment of **VI** as the product of a similar photoconversion of the pyrazolylborate ligand from bidentate to unidentate on high energy photolysis of **IV**.



(VII)

The photoreactions of **I** and **IV** in CH_4 matrices were the same as in argon matrices (Table 2). The photoreactions were, however, observed to be faster in CH_4 compared with argon matrices [15]. The lack of C–H activation photoproducts, *e.g.* $Rh(HBPz_3^*)(CO)(CH_3)(H)$ which was observed in solution [5], was extremely surprising.

3.2. Photolysis of IV and I in N_2, CO and ^{13}CO doped matrices

The IR spectrum of **IV** isolated at high dilution in an N_2 matrix is shown in Fig. 4(a). Short periods of photolysis (filter D) resulted in the production of two new terminal CO-stretching bands, of differing intensities, at 2026.7 (medium) and 2003.2 (weak) cm^{-1}, a band for "free" CO and a further new band at 2243.0 cm^{-1}, all at the expense of the parent IR bands (Fig. 4(b)). Extended photolysis with filter D afforded increases in the new bands at 2243.0 and 2026.7 cm^{-1} along with the growth of the "free" CO band, while the new band at 2003.2 cm^{-1} remained fairly constant in intensity. Photolyses with higher energy light (filter A) produced further spectral changes: another new band appeared at 2105.3 cm^{-1}, the band centred at 2026.7 cm^{-1} became considerably stronger and broader and all the other new bands continued to grow (Fig. 4(c)). A final period of low energy irradiation (filter E) produced some photochemical reversal, with the parent bands growing at the expense of the bands at

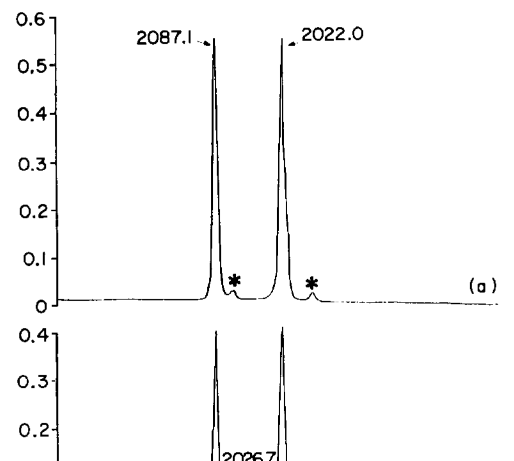


Fig. 4. IR spectra (Nicolet 7199 FTIR, 1 cm^{-1} resolution) from an experiment with **IV** isolated at high dilution in an N_2 matrix: (a) after deposition, (b) after 30 min irradiation (filter D), (c) after 30 min irradiation (filter A), (d) after further 2 h irradiation (filter E), and (e) subtraction spectrum ((d) − *C*(c)) where *C* is a scaling factor. Bands marked * arise from $Rh(H_2BPz_2^*)(^{12}CO)(^{13}CO)$ present in natural abundance.

2243.0, 2139.1 ("free" CO), 2026.7 and 2003.2 cm^{-1} (Figs. 4(d) and 4(e), Table 2).

Low energy photolysis of **IV** has again produced the CO-loss product **V** (ν(CO) at 2003.2 cm^{-1} in an N_2 matrix), which underwent photoreversal to **IV**, as observed in argon and CH_4 matrices. In addition, two further bands were produced on photolysis with filter D, at 2243.0 and 2026.7 cm^{-1}. At this wavelength of irradiation these bands were unique to N_2 matrices, and can probably be assigned to the ^{14}N–^{14}N and CO-stretching modes of $Rh(H_2BPz_2^*)(CO)(N_2)$ (**VIII**) respectively. The observed photoreversal of **VIII** to **IV** is analogous with the behaviour of $Rh(L)(CO)(N_2)$ (L = acetylacetonate, 1,1,1-trifluoroacetylacetonate or hexafluoroacetylacetonate) complexes [13], $M(\eta^5\text{-}C_5H_5)(CO)(N_2)$ (M = Ir or Rh; R = H or CH_3) complexes [3], $Fe(\eta^4\text{-}C_4H_4)(CO)_2(N_2)$ [17] and $Ni(CO)_3(N_2)$ [18] which have ν(NN) about or above 2200 cm^{-1}, and is in contrast to observations for dinitrogen complexes $Co(\eta^5\text{-}C_5H_5)(CO)(N_2)$ [19] and $Mn(\eta^5\text{-}C_5H_5)(CO_2)(N_2)$ [17] which have ν(NN) well below 2200 cm^{-1} and show no thermal or photochemical reversal.

On higher energy photolysis a further new band was seen at 2105.3 cm^{-1} with a considerable growth and broadening of the band at 2026.7 cm^{-1}, which corresponds to the CO-stretching mode of **VIII**. It seems that **VI** produced on high energy photolysis in argon and CH_4 has once more been produced, but the lower wavenumber IR band of **VI** (*ca.* 2025 cm^{-1}) is close to the CO-stretching band of **VIII** already present, thus resulting in broadening of the observed band.

The IR spectrum of **IV** isolated at high dilution in CO matrices showed two bands similar to those observed in argon, CH_4 and N_2 matrices (Table 2). Prolonged photolysis (6 h) at various wavelengths (filters D, H and A) resulted in no clear spectral changes. No evidence was found for the formation of an expanded coordination species such as $Rh(\kappa^1\text{-}H_2BPz_2^*)(CO)_3$ in the CO matrix. This is in contrast to results obtained for two other dicarbonyl species, $Co(\eta^5\text{-}C_5H_5)(CO)_2$ [19] and $Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)$ [20], which gave $Co(\eta^3\text{-}C_5H_5)(CO)_3$ and $Fe(\eta^3\text{-}C_5H_5)(CO)_3(CH_3)$ respectively. However, a fairly stable 16-electron species, $Rh(acac)(CO)_2$, also did not undergo an associative reaction with CO when photolysed in CO matrices [13].

The IR spectrum of **IV** isolated at high dilution in a ^{13}CO doped (10%) CH_4 matrix showed the two strong symmetric and asymmetric bands of the di-^{12}CO species together with two weak bands due to natural abundance $Rh(H_2BPz_2^*)(^{12}CO)(^{13}CO)$. Irradiation (filter D) of the matrix caused rapid growth of the bands corresponding to $Rh(H_2BPz_2^*)(^{12}CO)(^{13}CO)$ and $Rh(H_2BPz_2^*)(^{13}CO)_2$, as confirmed by the satisfactory agreement between the observed and calculated [19–21] band positions (Table 3) for a C_{2v} $M(CO)_2$ fragment. Further photolysis gave the ^{13}CO-enrichment product band corresponding to the ^{12}CO band previously assigned to the monocarbonyl species **V**. The good correspondence between the observed and calculated band positions (Table 3) of the Rh(CO) fragment confirms the assignment of the band to **V**.

Due to the low conversion to **VI** on higher energy photolysis, it was not possible to produce any data to aid in the identification of this species via ^{13}CO force-field fitting procedure.

Periods of photolysis (filters D, B and A) of **I** in N_2 matrices all resulted in the production of **VII**, (ν(CO) at 2088.2 and 2020.2 cm^{-1}). No evidence was found for either a dinitrogen containing species being produced on photolysis, unlike photolysis of **IV** in N_2 matrices which resulted in the production of **VIII**, or the monocarbonyl species **III**, produced in small quantities in argon and CH_4. Subsequent long wavelength photolysis (filter E) produced no further spectral changes.

Photolysis (filter D) of **I** in pure CO matrices resulted in the production of the bidentate pyrazolyborate species **VII** (ν(CO) at *ca.* 2085 and 2028.6 cm^{-1}, the exact position of the band at 2085 cm^{-1} is not quoted as it is a shoulder on a fairly broad host matrix IR band: ν(CO) of $^{13}C^{16}O$ is *ca.* 2090 cm^{-1}). However, not unexpectedly, the formation of the CO-loss species **III** was not observed in CO matrices. Higher energy photolyses (filters B and A) only resulted in further **VII** being produced. No evidence was found for any products of associative reactions with the CO matrix, such as $Rh(\kappa^2\text{-}HBPz^*_3)(CO)_3$, being formed at any stage of the experiments.

The IR spectrum of **I** isolated at high dilution in a ^{13}CO doped (10%) CH_4 matrix showed the two strong bands of the di-^{12}CO species together with the weaker two bands of $Rh(HBPz^*_3)(^{12}CO)(^{13}CO)$ in natural abundance. Irradiation (filter D) produced **VII** (ν(CO) at 2086.1 and 2019.3 cm^{-1}) and caused a minimal growth in the bands corresponding to $Rh(HBPz^*_3)(^{12}CO)(^{13}CO)$. Further photolysis only resulted in continued production of **VII** and very little conversion of the di-^{12}CO parent complex to the ^{13}CO substituted species. This is in contrast to **IV** where extensive incorporation of ^{13}CO occurred on photolysis in ^{13}CO doped matrices. Even though **VII** was produced in fairly generous amounts, no bands were observed that might be due to ^{13}CO incorporation into **VII**. It is once more apparent that **VII** is fairly stable and does not participate in further photochemical reactions after its production.

3.3. Photolysis of I in other media at 12–298 K

Photolysis of **I** in a perfluorokerosine (PFK) mull (ν(CO) at 2054 and 1981 cm^{-1}) at 12 K with filter E yielded no photoproducts. (Perfluorokerosine was chosen as an "inert medium", *cf.* the use of argon for "inert" gas matrices). However, a similar photolysis at 77 K afforded new bands at 2033 (m, sh) and 1961 (m, sh) cm^{-1} while the parent bands decreased slightly.

Photolysis of **I** in Nujol mulls (ν(CO) at 2054 and 1981 cm^{-1} gave similar results (Nujol mulls have been shown to be photoreactive at 12 K undergoing C–H activation in the presence of $Ir(\eta^5\text{-}C_5R_5)(CO)_2$ (R = H and Me) [22]). Additional new bands appeared at 77 K at 2134 cm^{-1} ("free" CO), 2037 (m, sh, br) and 1962 (m, sh) cm^{-1}. At 298 K the photolysis (filter E) caused a marked decrease in the parent bands and new bands were observed at 2037 (m), 2029 (ms) and 2006 (mw) cm^{-1} (Table 2).

Dispersal of **I** into paraffin wax discs, which are also a potential source of C–H bonds for C–H photoactivation by metal complexes, afforded bands at 77 K which can be assigned to **I** (ν(CO) at 2055 and 1974 cm^{-1}) together with weak bands at 2150, 2121, 2113, 2017, 2003, 1901 and 1896 cm^{-1}. The presence of the weak bands indicates that some decomposition has occurred. (In order to prepare wax discs it was necessary to heat the sample with wax before casting the disc as a film on the spectroscopic window. Since **I** is thermally sensitive it was always likely that some decomposition might occur.) Surprisingly, photolysis (filter E and others too) produced no new bands.

Given the correspondence in the terminal CO stretching bands for PFK mulls (ν(CO) at 2033 and 1961 cm^{-1}) at 12 K with those for Nujol mulls (ν(CO) at 2037 and 1962 cm^{-1}) at 12 K, it might be supposed that a new $Rh(CO)_2$ containing species had been formed. However, the observation of "free" CO in the case of Nujol mulls and the fact that bands are detected at 2037, 2029 and 2006 cm^{-1} for Nujol at 298 K without a band at *ca.* 1960 cm^{-1} indicates that the bands at *ca.* 2030 cm^{-1} and *ca.* 1960 cm^{-1} belong to different species. Indeed, the latter band can be correlated with the gas matrix data for the monocarbonyl species **III** (Table 2). This is supported by the observation of "free" CO in Nujol experiments.

At 77 K and 298 K the additional bands at 2037 and 2037–2029 cm^{-1} in the Nujol experiments can be correlated with bands observed on photolysis of **I** in benzene (2049 cm^{-1}) and hexane (2028 cm^{-1}) where

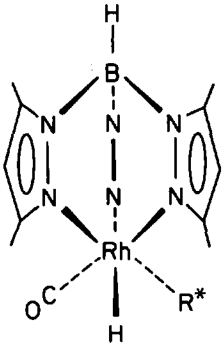
$$\begin{tikzcd}
\mathrm{Rh(HPBz^*_3)(CO)_2}\ (\mathrm{I}) \arrow[r, shift left, "\text{(i), }-\mathrm{CO}"] \arrow[d, "\text{(i)}"] & \mathrm{Rh(HBPz^*_3)(CO)}\ (\mathrm{III}) \arrow[l, shift left, "\text{(ii), }+\mathrm{CO}"] \arrow[r, "+{}^{13}\mathrm{CO}"] & \mathrm{Rh(HBPz^*_3)(^{12}CO)(^{13}CO)} \\
\mathrm{Rh(\kappa^2{-}HBPz^*_3)(CO)_2}\ (\mathrm{VII}) & &
\end{tikzcd}$$

(i) $h\nu$, $330 < \lambda < 390$ nm

(ii) $h\nu$, $\lambda > 375$ nm

Scheme 2.

C–H activation has demonstrably occurred [5,12]. It seems probable, therefore, that C–H activation has occurred at 77 K and that one of the new species corresponds to **IX**. The precedent for such C–H activation has been clearly established from the photolysis of $[\mathrm{Ir}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]$ (R = H, Me) complexes in Nujol mulls [22] as well as in $\mathrm{CH_4}$ matrices [3].



R* = carbon skeleton of Nujol

(IX)

The 2033 $\mathrm{cm^{-1}}$ band in the perfluorokerosine mull experiment can perhaps be attributed to the fact that when hydrocarbons are fluorinated there may be incomplete fluorination (*ca.* 99%) and hence there are some residual C–H bonds which could be activated. Experiments with poly(vinyl chloride) films containing residual tetrahydrofuran (THF, a few percent) have shown that coordinatively unsaturated metal species will efficiently scavenge THF molecules at 77 K to form complexes [23]. Hence it is feasible that residual C–H bonds could be activated by photolysing **I** in perfluorokerosine. The origin of the weak band at 2006 $\mathrm{cm^{-1}}$ is not clear.

It is significant that no C–H activation occurs at *ca.* 12 K but that on warming to 77 K the species which are trapped can afford C–H activation and that such activation is facile at 298 K.

4. Discussion

Photochemical reactions observed for **I** and **IV** in frozen gas matrices are summarized in Schemes 2 and 3 respectively. Photolysis into the lowest electronic absorption band of **I** produced two new species: one, the product of a tridentate to bidentate conversion of the tris-pyrazolylborate ligand, **VII**, and the second, the CO loss product **III**, formed in trace amounts. Although the UV spectrum of **I** is unassigned, it seems reasonable to assign the lowest energy electronic transition to a d–d transition on the basis of the extinction coefficient with perhaps some tailing of the higher energy charge-transfer band into the visible. Excitation into the d–d band will populate σ^* levels and lead to dissociation of CO and N ligands. The higher yield of **VII** over **III** may reflect the fact that the CO once ejected can be mobile within the matrix cage and recombine with the Rh whereas the N donor will be less mobile because it is part of the pyrazolylborate framework. Higher energy photolysis of **I**, involving the charge-transfer band may result in more CO being produced if only because the ejected CO will have higher thermal energy and will be displaced further from the Rh in the matrix cage. The UV spectrum of **IV** also remains unassigned although again it seems likely from the data in Table 1 that the lowest energy electronic transition is a d–d transition. Photolysis into this band labilizes a CO ligand. Higher energy photolysis could effect the conversion of the bis-pyrazolylborate ligand from bidentate to unidentate, *i.e.* the formation of **VI**, by populating the state leading to N ligand ejection with sufficient energy to overcome the limitations of the cage.

From the matrix experiments it seems probable that the facile tridentate ⇌ bidentate interconversion, *i.e.* **I** ⇌ **VII**, speculated by Ghosh and Graham [5] as a possible route to the high efficiency for the CH pho-

$$\begin{tikzcd}
\mathrm{Rh(H_2BPz_2^*)(CO)_2}\ \textbf{(IV)} \arrow[r, "\text{(ii)}"] \arrow[d, shift left, "\text{(i), }-\mathrm{CO}"] & \mathrm{Rh(\kappa^1{-}H_2BPz_2^*)(CO)_2}\ \textbf{(VI)} \\
\mathrm{Rh(H_2BPz_2^*)(CO)}\ \textbf{(V)} \arrow[u, shift left, "\text{(iii), }+\mathrm{CO}"] \arrow[r, shift left, "+\mathrm{N_2}"] \arrow[d, shift left, "+{}^{13}\mathrm{CO}"] & \mathrm{Rh(H_2BPz_2^*)(CO)(N_2)}\ \textbf{(VIII)} \arrow[l, shift left, "\text{(iii), }-\mathrm{N_2}"] \\
\mathrm{Rh(H_2BPz_2^*)(^{12}CO)(^{13}CO)} \arrow[u, shift left, "-{}^{13}\mathrm{CO}"] \arrow[r, shift left, "-{}^{12}\mathrm{CO}"] & \mathrm{Rh(H_2BPz_2^*)(^{13}CO)} \arrow[l, shift left, "+{}^{12}\mathrm{CO}"]
\end{tikzcd}$$

(i) $h\nu$, $330 < \lambda < 390$ nm

(ii) $h\nu$, $\lambda < 330$ nm

(iii) $h\nu$, $\lambda > 375$ nm

Scheme 3.

toactivation by **I** in room temperature solvents, does indeed take place. In fact Graham and coworkers have observed [12] that the IR spectrum of **I** recorded in CH_2Cl_2 has two unexpected very weak bands at 2080 and 2011 cm^{-1}, as well as the expected two strong bands at 2054 and 1961 cm^{-1}. Allowing for shifts in band positions due to temperature change and the different environment of a frozen gas matrix compared with organic solvents, it seems likely that the weak bands observed by Graham correspond to a small amount of **VII** (ν(CO) at 2086.1 and 2017.9 cm^{-1} in argon) being present in the solution. It is proposed that the interconversion $\mathbf{I} \rightleftharpoons \mathbf{VII}$ may exist as an equilibrium in CH_2Cl_2 at room temperature, and that at 12 K in gas matrices the conversion of **I** to **VII** may be taking place photochemically. It is perhaps surprising that this conversion cannot be reversed photochemically in the gas matrices although the existence of **IV** as an air-stable 16-electron compound perhaps suggests the observed stability of **VII**. The stabilizing effect of methyl substituents on the pyrazolyl rings has been utilized in the synthesis of a number of stable polypyrazolylborate organometallic compounds with non-inert gas configurations [24,25]. The photoproduct **VII** might be expected to have been photoreactive itself as **IV** underwent both photochemical CO loss and bidentate to unidentate photoconversion. However, this does not appear to be the case and perhaps this is due to steric factors involving the "labile" pyrazolyl ring of **VII**.

There was no evidence for the photochemical activation, by **I** of C–H bonds of the methane matrix at 12 K, even though **I** has been shown to activate alkane C–H bonds with high quantum efficiency in room temperature solutions. The chemistry of tris-pyrazolylborate complexes frequently resembles that of cyclopentadienyl (or pentamethylcyclopentadienyl) complexes [4] and as $[M(\eta^5\text{-}C_5R_5)(CO)_2]$ ($R = H$ or CH_3, M = Rh or Ir) complexes have conclusively been shown [15] to photoactivate methane C–H bonds even at 12 K it is unusual that no methane activation by **I** was observed in the matrix. The production of **III** and **VII** in the gas matrices has been proposed, both of these species are possible reaction intermediates in C–H activation processes, but at 12 K no activation was observed. This shows that a thermal step is likely to be required for the activation of C–H bonds by **I**. Photolysis produces the "reactive" intermediates but thermal energy is required to produce the final products of the reaction. This seems to be supported by the photolysis experiments using PKK and Nujol mulls which have a wider thermal range than argon and CH_4 matrices which evaporate at *ca.* 50 K. It is also possible that the steric factors involved with the tridentate to bidentate conversion are a hindrance to the C–H activation proceeding at low temperatures.

It should be noted that observation of regions of the IR spectra of **I** and **IV**, apart from the carbonyl-stretching region, were not used in positive identification of the photoproducts as little spectral changes were observed on photolysis. (Trofimenko has published the IR spectra of $M(H_2BPz_2)_2$, $M(HBPz_3)_2$ and $M(BPz_4)_2$ (M = Fe, Co, Ni, Cu and Sn; Pz = the unsubstituted pyrazolyl ring) in the region 4000–650 cm^{-1}. The skeletal IR modes were all very complex, spectral differences were difficult to observe and the spectra remain unassigned [26]. The M–N stretching bands of $Fe(HBPz_3^*)_2$ and other similar polypyrazolylborates have been observed and assigned in the region below 400 cm^{-1} [27]. Because of the general weakness of such bands, no measurements were made in this region for **I** and **IV** and their photoproducts.)

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