Organic Matrix Photochemical Studies of Rhenacarborane Nitrosyl Complexes. Evidence for Linkage Isomeric Nitrosyl Photointermediates

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The photochemistry of the rhenacarborane nitrosyl compounds [1,2-R_2-3,3-$(CO)_2$-3-NO-*closo*-3,1,2-$ReC_2B_9H_9$], where R = H, **I**, and R = Me, **II**, has been studied in Nujol and methytetrahydrofuran (MeTHF) frozen glasses at ca. 90 K. Visible light photolysis gives rise to a new species that has been assigned to the isonitrosyl linkage isomer, while ultraviolet photolysis gives rise to a second species believed to be the η^2-NO linkage isomer. In MeTHF high-energy photolysis also gives rise to a CO-loss product. Photolysis of derivatives of **I**, [3-L-3-L′-3-NO-*closo*-3,1,2-$ReC_2B_9H_{11}$], where L = CO, L′ = PMe_3, **III**; L = CO, L′ = CNC_6H_3-Me_2-2, 6, **IV**, and L = L′ = $CNC_6H_3Me_2$-2,6, **V**, all give rise to a photoproduct believed to be the η^2-NO lnkage isomer. There was no evidence of the isonitrosyl isomer in these cases. Complexes **III** and **IV** also undergo CO loss. Ultraviolet photolysis of [3,3,3-$(CO)_3$-*closo*-3,1,2-$RuC_2B_9H_{11}$], **VI**, in MeTHF results in CO loss and formation of the corresponding [3,3-$(CO)_2$-3-MeTHF-*closo*-3,1,2-$RuC_2B_9H_{11}$] derivative. In frozen Nujol, ultraviolet photolysis of **VI** gives rise to a CO-loss species. Upon visible light back-photolysis or annealing of the sample, this photoproduct gives rise to a second dicarbonyl species of unknown structure.

Rest and co-workers have examined the photochemistry of a number of metal nitrosyl derivatives in gas matrixes at 12 K.[1] The results of these studies have been interpreted to suggest that a relatively low energy process (600 nm in the case of $Mn(CO)(NO)_3$) results in photoelectron transfer from the metal to the NO, yielding an $[Mn(CO)(NO)_2]^+NO^-$ ion pair.[2] For example, photolysis of [Ni(NO)(η^5-C_5H_5)] resulted in disappearance of the NO stretching band at ca. 1834 cm^{-1} and the appearance of a new band at 1390 cm^{-1}. Free NO[3] absorbs at 1880 cm^{-1}, while NO^- absorbs between 1375 and 1350 cm^{-1} depending upon the counterion.[4] Recognizing the ambiguities of the bonding between the two ions, Rest designated these groups as NO*.

Elegant photocrystallographic work by Coppens and co-workers has shown that the excited state species for [Ni(NO)(η^5-C_5H_5)] is [Ni(η^2-NO)(η^5-C_5H_5)].[5] Indeed, photocrystallographic studies of $Na_2[Fe(CN)_5(NO)]$[6] and $K_2[Ru(OH)(NO_2)_4(NO)]$[7] have established both η^2-NO and isonitrosyl linkage isomers in the excited state species. In keeping with these observations, the photointermediates of ruthenium nitrosyl porphyrins have been assigned to linkage isomers.[8] These studies have been reviewed.[9]

Recent work in the Stone laboratory has resulted in the synthesis of a series of rhenacarborane nitrosyl derivatives which have proven to be interesting and informative subjects for organic matrix photochemistry.[10] The results of these studies along with our examination of the photochemistry of the closely related ruthenacarborane tricarbonyl are reported in this paper. In later papers in this series we shall examine the photochemistry of a series of tris(pyrazoyl)borate group VI dicarbonyl nitrosyl derivatives and revisit the photochemistry of the cyclopentadienyl group VI dicarbonyl nitrosyl compounds that Rest has briefly examined.[11]

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Table 1. Electronic Spectra

compound	THF	petroleum ether	CH_2Cl_2
[1,2-Me_2-3,3-$(CO)_2$-3-NO-*closo*-3,1,2-$ReC_2B_9H_9$], **II**	428 sh (190)	410 sh	410 sh
	348 (580)	352	348
[3-CO-3-PMe_3-3-NO-*closo*-3,1,2-$ReC_2B_9H_{11}$], **III**	452[a]		
	380 sh		
	332 sh		
[3-CO-3-CNR-3-NO-*closo*−3,1,2-$ReC_2B_9H_{11}$], **IV**	452[a]		
	380		
[3,3-$(CNR)_2$-3-NO-*closo*−3,1,2-$ReC_2B_9H_{11}$], **V**	443 (640)		
	290 (3950)		
[3,3,3-$(CO)_3$-*closo*-3,1,2-$RuC_2B_9H_{11}$], **VI**	500 (210)		
	380 sh (640)		

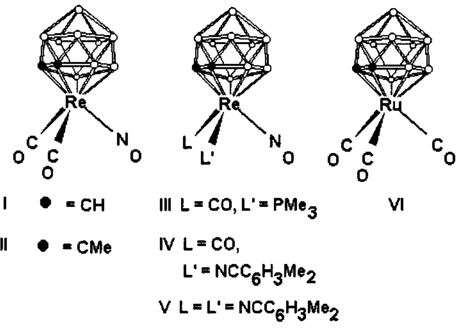
[a] Insufficient sample for molar absorbtivity measurement. λ_{max} (ϵ, M^{-1} cm^{-1}).

Table 2. IR Spectra of I−IV and Photofragments in Organic Matrixes at ca. 90 K[a]

compound	Nujol	MeTHF
[1,2-Me_2-3,3-$(CO)_2$-3-NO-*closo*-3,1,2-$ReC_2B_9H_9$], **II**	2089	2090
	2034	2033
	1762	1778
[1,2-Me_2-3,3-$(CO)_2$-3-ON-*closo*-3,1,2-$ReC_2B_9H_9$], **IIa**	2056	2053
$\lambda_{irr} = 450 \pm 70$ nm	2001	2095
	1612	1655
[1,2-Me_2-3,3-$(CO)_2$-3-(η^2-NO)-*closo*-3,1,2-$ReC_2B_9H_9$], **IIb**	2079	2078
$\lambda_{irr} < 450$ nm	2014	2017
[1,2-Me_2-3-(CO)-3-MeTHF-3-NO-*closo*-3,1,2-$ReC_2B_9H_9$], **IIc**		1991
		1727
[3-CO-3-PMe_3-3-NO-*closo*-3,1,2-$ReC_2B_9H_{11}$], **III**		1994
		1724
[3-CO-3-PMe_3-3-(η^2-NO)-*closo*-3,1,2-$ReC_2B_9H_{11}$], **IIIa**		1949
[3-MeTHF-3-PMe_3-3-NO-*closo*-3,1,2-$ReC_2B_9H_{11}$], **IIIb**		1671
[3-CO-3-CNR-3-NO-*closo*-3,1,2-$ReC_2B_9H_{11}$], **IV**		2173
		2024
		1753
[3-CO-3-CNR-3-(η^2-NO)-*closo*-3,1,2-$ReC_2B_9H_{11}$], **IVa**		2154
		1977
[3-MeTHF-3-CNR-3-NO-*closo*−3,1,2-$ReC_2B_9H_{11}$], **IVb**		2112
		1691
[3,3-$(CNR)_2$-3-NO-*closo*−3,1,2-$ReC_2B_9H_{11}$], **V**		2159
		2122
		1719
[3,3-$(CNR)_2$-3-(η^2-NO)-*closo*-3,1,2-$ReC_2B_9H_{11}$], **Va**		2167
		2128
[3,3,3-$(CO)_3$-*closo*-3,1,2-$RuC_2B_9H_{11}$], **VI**	2108	2117
	2055	2063
	2043	2052
[3,3-$(CO)_2$-*closo*-3,1,2-$RuC_2B_9H_{11}$], **VIa**	2064	
	2017	
[3,3-$(CO)_2$-*closo*-3,1,2-$RuC_2B_9H_{11}$] (anneal), **VIb**	2083	
	2042	
[3,3-$(CO)_2$-3-MeTHF-*closo*−3,1,2-$RuC_2B_9H_{11}$], **VIc**		2043
		1993

[a] All values are ± 2 cm^{-1}.

Results and Discussion



Electronic spectra of **I** and **II** were identical. Both compounds had a well-defined medium intensity band ($\epsilon = 576$) at 348 nm with a long-wavelength shoulder at 428 nm ($\epsilon = 188$) that was found to tail to at least 520 nm, Table 1. An intense band rose off-scale at 290 nm. Band positions were essentially identical in petroleum ether, THF, and CH_2Cl_2.

Photochemical studies of **I** and **II** were carried out in frozen Nujol at ca. 90 K, while **II** was also examined in 2-methyltetrahydrofuran, MeTHF, glass at ca. 90 K. Positions of the carbonyl and nitrosyl IR bands are presented in Table 2. The carbonyl and nitrosyl stretching frequencies of **I** and **II** were almost identical in Nujol, and thus only the values for **II** are reported. The carbonyl stretching frequencies of **II** were almost identical in Nujol and MeTHF, but the nitrosyl stretching frequency was shifted to higher energy in MeTHF. The IR spectrum of **II** in MeTHF at ca. 90 K is presented in Figure 1a.

Photolysis at wavelengths greater than 500 nm had no discernible effect on the spectra of the compounds; however, photolysis into the low-energy shoulder at

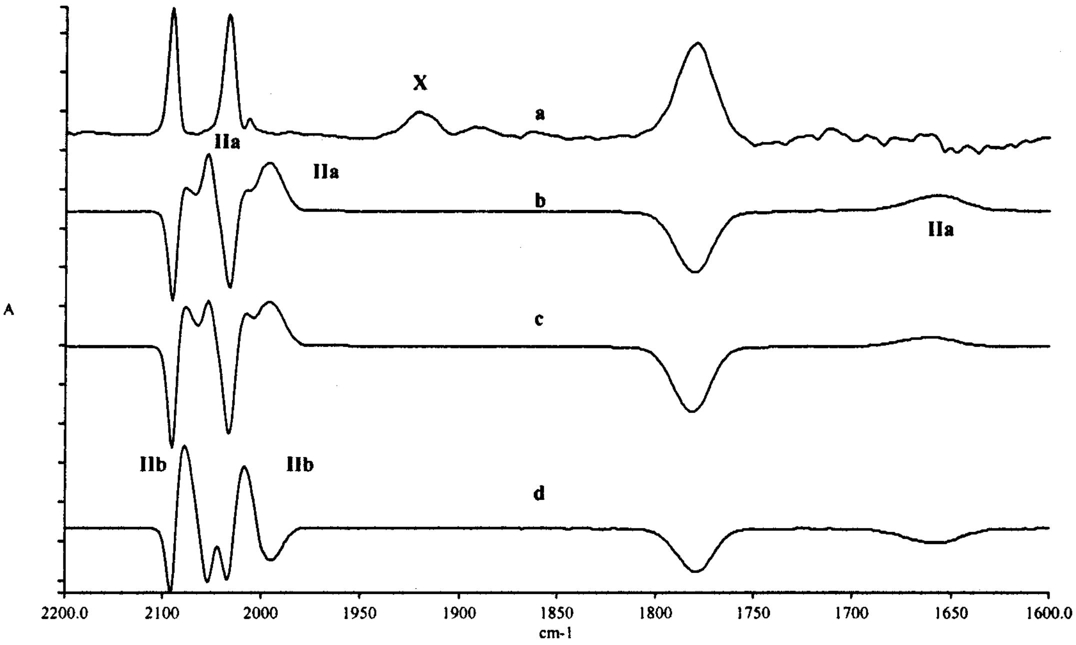


Figure 1. Photolysis of [1,2-Me_2-3,3-$(CO)_2$-3-NO-closo-3,1,2-$ReC_2B_9H_9$], **II**, in MeTHF glass at ca. 90 K: (a) sample prior to photolysis, (b) difference spectrum 10 min photolysis at $\lambda_{irr} = 450 \pm 70$ nm minus (a), (c) difference spectrum 10 min photolysis at $\lambda_{irr} = 400 \pm 70$ nm minus 10 min photolysis at $\lambda_{irr} = 450 \pm 70$ nm, (d) difference spectrum.

$\lambda_{irr} = 450 \pm 70$ nm resulted in a bleaching of the bands associated with the starting materials and growth of new bands in both the carbonyl and nitrosyl regions. For **II** these new bands were observed at 2056, 2001, and 1612 cm^{-1} in Nujol and at 2053, 2095, and 1655 cm^{-1} in MeTHF, Figure 1b. Small features are observed at 2078 and 2017 cm^{-1} in MeTHF. Continued photolysis at $\lambda_{irr} = 400 \pm 70$ nm resulted in the bands of the starting material and the new bands decreasing in intensity, while a new pair of carbonyl bands were found to grow in at 2079 and 2014 cm^{-1} in Nujol and 2078 and 2017 cm^{-1} in MeTHF, Figure 1c. Continued photolysis, 350 nm < λ_{irr} < 400 nm, resulted in the bands of the starting material and the initial photoproduct decreasing while the bands of the second photoproduct increased, Figure 1d. Both the first and second photochemical events could be reversed to re-form starting materials by either back photolysis, λ_{irr} > 650 nm, or annealing (for Nujol) of the matrix to ca. 135 K. Repeated attempts to locate an IR band that might be attributed to nitrosyl for the second photointermediate were unsuccessful. Photolysis of a ^{15}NO-labeled sample of **II** yielded results that were consistent with the formation of two intermediates, and again no nitrosyl band could be observed for the second photointermediate. Photolysis of **II** in MeTHF, 330 nm < λ_{irr} < 400 nm, resulted in the appearance of a band attributable to free CO and new bands at 1991 and 1727 cm^{-1}.

The observed behavior is consistent with the formation of two distinct photointermediates in which no CO is lost and a third intermediate in MeTHF involving loss of CO and probably complexation with MeTHF. Loss of NO can also be ruled out since there was no band observed at 1880 cm^{-1}. The first photoproduct, **IIa**, is associated with the electronic band at 428 nm, while the second photoproduct, **IIb**, appears to be related to the 348 nm band. In keeping with the observations of Coppens, we assign **IIa** to an isonitrosyl linkage isomer, Figure 2b, while the second, **IIb**, is assigned to an η^2-NO species, Figure 2c. The η^2-NO stretching band of this latter species is likely hidden beneath the strong solvent C−H bending bands in the 1500−1300 cm^{-1} region (vide infra). The bands observed upon high-energy photolysis in MeTHF are consistent with a CO-loss species, [3-CO-3-MeTHF-3-NO-*closo*-3,1,2-$ReC_2B_9H_{11}$], **IIc**. It is possible that CO loss occurs in Nujol, but that at 90 K there is sufficient kinetic energy to allow CO recapture.

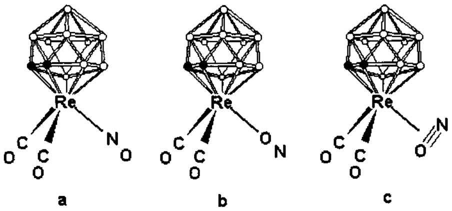


Figure 2. Linkage isomers of **I** and **II**: (a) nitrosyl, (b) isonitrosyl, (c) η^2-nitrosyl.

There is no evidence for the formation of NCO ligands upon high-energy photolysis, as has been reported by Knox[12] and Rest[11] for [$M(CO)_2(NO)(\eta^5$-$C_5H_5)$], where M = Mo or W, respectively. This aspect of the photochemistry of the group VI nitrosyl derivatives will be dealt with in some detail in a future publication in this series.

To further examine the behavior of these rhenacarborane species, we have examined the matrix photochemistry of three derivatives of **I**. The complex [3-CO-3-NO-3-PMe_3-*closo*-3,1,2-$ReC_2B_9H_{11}$], **III**, was taken up in MeTHF and the sample frozen to ca. 90 K. **III** has IR bands at 1994 and 1724 cm^{-1} attributable to the carbonyl and nitrosyl ligands, respectively. Photolysis of this sample, 550 nm < λ_{irr} < 400 nm, resulted in bleaching of the starting material bands and growth of a new band at 1949 cm^{-1}. No band attributable to the

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Table 3. NO Stretching Frequencies (in cm^{-1}) for Nitrosyl Linkage Isomers in Representative Compounds

compound	M−NO	M−ON	M−η^2-NO	ref
$(C_5H_5)NiNO$	1834		1390	1e, 1f
$[Fe(CN)_5(NO)]^{2-}$	1950	1835	1666	6, 13
$(OEP)Ru(NO)(O\text{-}i\text{-}C_5H_{11})^a$	1791	1645	1493	8

[a] OEP = octaethylporphyrinato dianion.

nitrosyl was observed. Photolysis of this sample with long-wavelength light, $\lambda_{irr} > 500$ nm, resulted in clean reversal of the photoreaction. High-energy photolysis of a sample of **III**, 330 nm < λ_{irr} < 400 nm, resulted in the appearance of a band at 2131 cm^{-1} (free CO) and a new nitrosyl band at 1671 cm^{-1}.

Photolysis of [3-($CNC_6H_3Me_2$-2,6)-3-CO-3-NO-*closo*-3,1,2-$ReC_2B_9H_{11}$], **IV**, where $CNC_6H_3Me_2$-2,6 = 2,6-dimethylphenylisocyanide, in MeTHF yielded very similar results to those of **III**. Complex **IV** was found to have IR bands at 2173, 2024, and 1753 cm^{-1} attributable to the isocyanide, carbonyl, and nitrosyl ligands, respectively. Photolysis, $\lambda_{irr} = 400 \pm 70$ nm, resulted in bleaching of the bands of **IV** and growth of new bands at 2154 and 1977 cm^{-1}. Again, no band attributable to the nitrosyl could be identified. Photolysis at long wavelength cleanly reversed this process. Irradiation of a sample of **IV**, 330 nm < λ_{irr} < 400 nm, caused bands of both **IV** and the first photoproduct to decrease in intensity, while new bands at 2131 (free CO), 2112, and 1691 cm^{-1} were found to grow in.

Finally, [3,3-($CNC_6H_3Me_2$-2,6)$_2$-3-NO-*closo*-3,1,2-Re-$C_2B_9H_{11}$], **V**, was taken up in MeTHF. This compound was found to have bands at 2159, 2122, and 1719 cm^{-1} attributable to the two isocyanide and nitrosyl ligands. Photolysis, 330 nm < λ_{irr} < 450 nm, resulted in a decrease in the intensity of the bands of **V** and the appearance of new bands at 2167 and 2128 cm^{-1}. Back photolysis, $\lambda_{irr} > 450$ nm, cleanly reversed this photoreaction. No evidence was observed for loss of isocyanide, nor for a band that could be assigned to the NO in the photoproduct.

Comparison of the nitrosyl stretching frequencies of **III** and **IV** with **I** reveals that substitution of PMe_3 for a CO in **III** causes the nitrosyl stretching frequency to decrease by 55 cm^{-1}, while substitution with an isocyanide causes the nitrosyl stretching frequency to decrease by 26 cm^{-1}. Consistent with this, the CO-loss species generated by photolysis of **III** and **IV** have nitrosyl stretching frequencies 56 and 36 cm^{-1} below that of the CO-loss species of **II**. The similarity of nitrosyl stretching frequency shifts upon CO-loss of these three compounds argues that the nitrosyl ligand is similar in all three cases. In each case, **IIIb**−**Vb**, we assume these to be MeTHF-complexed species.

Compounds **III**−**V** all appear to undergo photolysis to form only an η^2-NO intermediate, **IIIa**−**Va**. No evidence for an isonitrosyl species was observed even with very careful control of the irradiation frequencies. As with **I** and **II**, the carbonyl stretching frequencies for the η^2-NO species of **III**−**IV** are all shifted to lower energy.

A comparison between the various nitrosyl vibrational bands of **I** and **II** and those of other nitrosyl compounds, Table 3, in which photochemical linkage isomerism is known or believed to be occurring is instructive. For **I** and **II** there is a 150 cm^{-1} (Nujol) and 120 cm^{-1} (MeTHF) shift to lower energy of the NO stretching frequency between the nitrosyl and isonitrosyl linkage isomers. The carbonyl bands decrease by about 34 cm^{-1}. For the ruthenium nitrosyl porphyrins the comparable shift is 146 cm^{-1}, while for the $[Fe(CN)_5(NO)]^{2-}$ ion the shift is 115 cm^{-1}.[13] The η^2-NO vibrational bands for the ruthenium nitrosyl porphyrins are shifted 294 cm^{-1} down in energy from those of the nitrosyl isomer, while this shift for the $[Fe(CN)_5(NO)]^{2-}$ anion is 284 cm^{-1}. The corresponding shift for [Ni(NO)(η^5-C_5H_5)] is 240 cm^{-1}. Assuming a comparable shift for **I** and **II**, we would anticipate an η^2-NO stretching frequency of about 1500 cm^{-1}, unfortunately coinciding with the C−H bending modes of Nujol or MeTHF. As we shall report later, η^2-NO bands can be observed for analogous nitrosyl compounds.

Finally, we note that the carbonyl stretching frequencies of **I** and **II** are sensors for the electronic consequences of changing the linkage isomerism of NO. Both the isonitrosyl and η^2-NO forms result in increases in back-bonding to the CO ligands with the isonitrosyl form producing the greater frequency shift to lower energies and presumably greater back-bonding.

In later work in this series we will demonstrate that similar patterns of behavior are exhibited by the group VI dicarbonyl nitrosyl derivatives of cyclopentadienyl and tris(pyrazolyl)borate.

In addition to the rhenacarborane derivatives described above we have examined the photochemistry of the ruthenacarborane compound [3,3,3-(CO)$_3$-*closo*-3,1,2-$ReC_2B_9H_{11}$], **VI**,[14] in both frozen Nujol and MeTHF matrixes. Under these conditions **VI** has three carbonyl stretching bands at 2108, 2055, and 2043 cm^{-1} in Nujol, Figure 3a. Irradiation at wavelengths longer than 400 nm were found to have no effect on the spectra of **VI**; however irradiation at 330 < λ_{irr} 400 nm resulted in CO loss (2130 cm^{-1}) to yield a species, **VIa**, with carbonyl bands at 2064 and 2017 cm^{-1}, Figure 3b. Back photolysis of the sample, $\lambda_{irr} > 535$ nm, or annealing results in reversal of the CO-loss process and growth of a new band at 2084 cm^{-1}, Figure 3c. Careful analysis of the relative intensities of the bands of starting material that grew in after either back photolysis or annealing suggests that the band at 2042 cm^{-1} very likely represents the overlap of a starting material band and a second band that we believe is related to the new band at 2084 cm^{-1}.

In MeTHF at 90 K, **VI** has three carbonyl stretching bands at 2117, 2063, and 2052 cm^{-1}. At room temperature in MeTHF only two bands are observed at 2111 and 2052 cm^{-1}. High-energy photolysis, 330 < λ_{irr} 400 nm, of **VI** in MeTHF gave rise to CO loss and formation of a new species with carbonyl bands at 2042 and 1993 cm^{-1}. The complex [3,3-(CO)$_2$-3-(THF)-*closo*-3,1,2-$ReC_2B_9H_{11}$] has been described, but the IR spectrum of this compound was not reported.[14] We have carried out the

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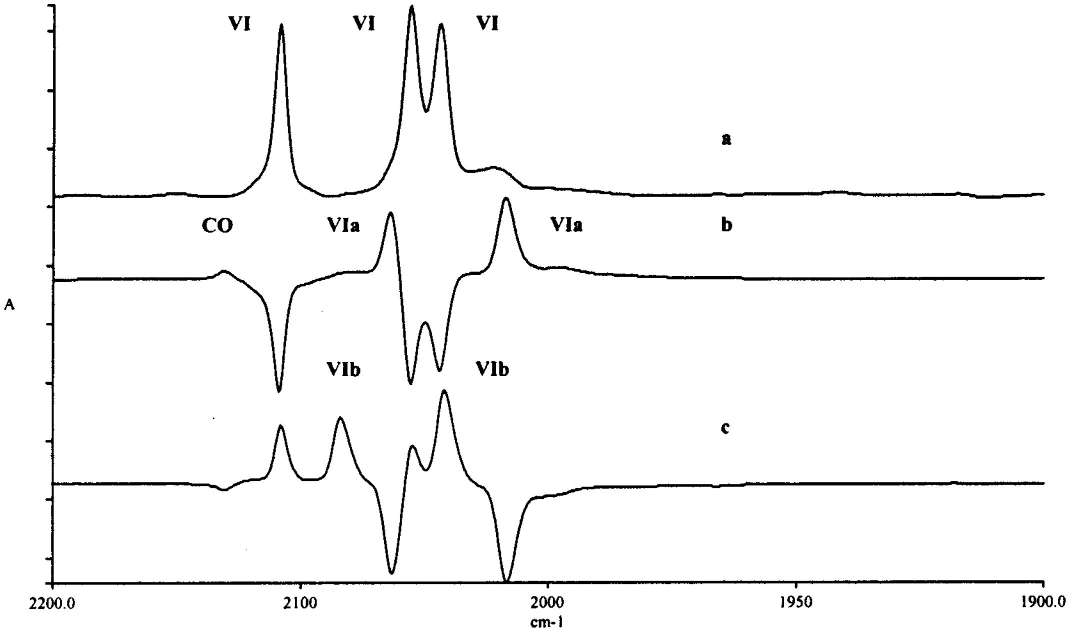

Figure 3. Photolysis of [3,3,3-$(CO)_3$-*closo*-3,1,2-$RuC_2B_9H_{11}$], **VI**, in Nujol glass at ca. 90 K: (a) sample prior to photolysis, (b) difference spectrum 75 min photolysis at 330 nm $< \lambda_{irr} <$ 400 nm minus (a), (c) difference spectrum 30 min photolysis at $\lambda_{irr} >$ 535 nm (back photolysis) minus 75 min photolysis at 330 nm $< \lambda_{irr} <$ 400 nm.

photolysis of **VI** in THF at room temperature and found that the resulting THF species has carbonyl stretching frequencies at 2031 and 1979 cm^{-1}. It is likely that the photoproduct, **VIc**, observed in MeTHF glass is [3,3-$(CO)_2$-3-(MeTHF)-*closo*-3,1,2-$ReC_2B_9H_{11}$].

The appearance of a second dicarbonyl species, **VIb**, upon back photolysis or annealing in Nujol is puzzling. Several papers have described the "plasticity" of the C−C bond of the carborane ring, and a series of structural distortions from the idealized *closo* structure have been reported.[15] These *pseudocloso* and *hypercloso* forms involve varying degrees of C−C bond breaking and M−B bond making. In these cases lengthening of the C−C bond is attributed to both steric and electron donor properties of substituents on the carbon atoms. In the present case there are no substituents on the carbons, but the metal in the CO-loss photoproduct is electron deficient, and this may result in a structural reorganization of the $RuC_2B_9H_{11}$ cluster. We deem it highly unlikely that C−H activation of Nujol might be responsible for the new bands since such an oxidative addition would yield a formally Ru(IV) species. The carbonyl stretching bands of a Ru(IV) species would be expected to be above those of **VI**.

Experimental Section

Compounds **I**−**VI** were prepared as described in the literature.[10,14] Electronic spectra were recorded on a Cary 2200 spectrometer. IR spectra were recorded using a Perkin-Elmer Spectrum 1000 FTIR spectrometer. IR spectra were recorded at 4 cm^{-1} resolution. Nujol matrix studies were carried out using a cryostat designed by Dr. A. Rest of the University of Southampton. MeTHF matrix studies were carried out using a Graseby Specac variable temperature cryostat. Photolyses were carried out using a 350 W high-pressure Hg lamp. Optical filters were used to control the wavelength ranges of the incident radiation.

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