



## Frozen matrix photolysis of Group VIII $M(\text{CO})_2\text{Cl}_2\text{L}_2$ derivatives: Direct observation of CO-loss species and photochemical isomerization

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### ARTICLE INFO

#### Article history:

Received 7 September 2007

Received in revised form 23 February 2008

Accepted 23 February 2008

Available online 4 March 2008

#### Keywords:

Group VIII complexes

Photolysis

Carbonyl ligand loss

Matrix photolysis

Bromide ion loss

### ABSTRACT

Photolysis of Group VIII complexes of the form  $M(\text{CO})_2\text{X}_2\text{L}_2$  and chelated ruthenium compounds,  $\text{Ru}(\text{CO})_2\text{Cl}_2(\kappa^2\text{-L})$  in frozen matrices results in CO loss. In the case of  $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PMe}_3)_2$  evidence is presented for photochemical bromide ion elimination.

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### 1. Introduction

Iron derivatives of the general form  $\text{Fe}(\text{CO})_2\text{X}_2\text{L}_2$ ,  $\text{L} = (\text{EtS})_2\text{C}_2\text{H}_4$  and *o*-phenanthroline, were first reported by Hieber and Bader in 1931 [1], only a few years after their report of the versatile  $\text{Fe}(\text{CO})_4\text{X}_2$  intermediates [2]. In the 1950s the Heiber group returned to this series of compounds, reporting the Group V derivatives of iron in 1956 [3], followed shortly by the analogous ruthenium series [4]. The osmium derivatives were reported in 1966 [5]. The sensitivity of these compounds to photochemical isomerism was first noted for the facile *cis* to *trans* transformation of  $\text{Fe}(\text{CO})_4\text{X}_2$  derivatives [6]. Subsequent to this, Pańkowski and Bigorgne [7] examined the solution photochemical isomerization of  $\text{Fe}(\text{CO})_2\text{X}_2(\text{PMe}_3)_2$ , where  $\text{X} = \text{Cl}, \text{Br}$  and  $\text{I}$ , and established that the *cis, cis, trans* isomer transforms to the *trans, trans, trans* (all-*trans*) isomer upon exposure to sunlight, while the temperature dependent back reaction occurred in the dark. Bellachioma et al. have used the photochemical transformation of *cis, cis, trans*  $\text{Fe}(\text{CO})_2\text{I}_2(\text{PMe}_3)_2$  for the synthesis of the all-*trans* isomer [8]. The analogous photochemical transformation of *cis, cis, trans*- $\text{Ru}(\text{CO})_2\text{-X}_2\text{L}_2$ , where  $\text{X} = \text{I}, \text{Br}$ , or  $\text{Cl}$  and  $\text{L} = \text{PR}_3$  or  $\text{AsR}_3$  has been reported by Mawby and coworkers [9].

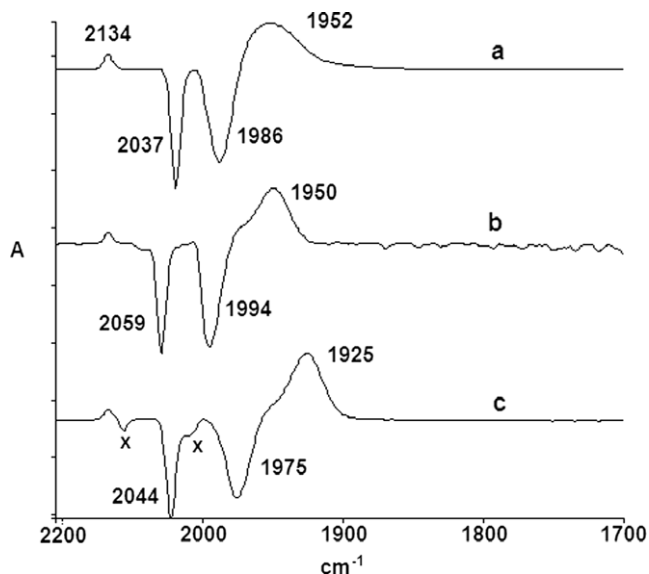
A unique feature of the ruthenium series of compounds is the isolation of 16 electron species such as  $\text{Ru}(\text{CO})_2\text{L}_2$  and  $\text{Ru}(\text{CO})\text{Cl}_2\text{L}_2$ ,

particularly for bulky phosphines. For example, Caulton and coworkers [10] have reported the reduction of  $\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}_2$ , where  $\text{L} = \text{P}(t\text{-Bu})_2\text{Me}$ ,  $\text{P}(i\text{-Pr})_3$ , and  $\text{PCy}_3$  to yield  $\text{Ru}(\text{CO})_2\text{L}_2$  derivatives. Bulky phosphines also stabilize derivatives of the form,  $\text{Ru}(\text{CO})\text{-Cl}_2\text{L}_2$  [11].

The solution photolysis of *cis, trans*- $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{bipy})$  and related substituted bipyridinyl derivatives has been examined by a number of groups who have established that 366 nm photolysis results in equatorial CO-loss [12]. In acetonitrile at room temperature the quantum yield for CO-loss is close to unity [12c]. The photophysics of *cis, trans*- $\text{Ru}(\text{CO})_2\text{I}_2(\text{bipy})$  has been examined by Lehtovuori et al. who assign the observed electronic bands to XLCT or  $\pi(\text{I}) \rightarrow (\text{Ru-I})\pi^*$  transitions [13]. Nieuwenhuis et al. have examined the electronic spectra of the analogous  $\text{Re}(\text{CO})_3\text{X}(\text{bipy})$  compounds and suggested that the nature of the emissive triplet state changes from  $^3\text{MLCT}$  to  $^3\text{XLCT}$  in the series,  $\text{Cl}, \text{Br}, \text{I}$  [14]. A similar suggestion was made by Luukkanen et al. for the excited states of  $\text{Ru}(\text{CO})_2\text{X}_2[4,4'-(\text{CO}_2\text{H})_2\text{bipy}]$ , where  $\text{X} = \text{Br}$  and  $\text{I}$  [15]. Photolysis of *cis, cis*- and *cis, trans*- $\text{Ru}(\text{CO})_2(\text{I})(\text{Me})(\text{bipy})$  has been shown to result in CO-loss [16]. The photolysis of *cis, trans*- $\text{Ru}(\text{CO})_2\text{X}_2(\text{bipy})$  has been studied by time-resolved IR methods by Gabrielsson et al. [17]. Significant to the current report, these workers were able to directly observe the CO-loss species within 2 ps of the 400 nm flash. Reaction of the CO-loss species with acetonitrile solvent was found to take place over about 13 ps to give the product with an equatorial CO and an axial acetonitrile ligand as observed in solution studies. The ultrafast (<1 ps) CO

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**Fig. 1.** Difference spectra of the photolyses of (a)  $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PPh}_2\text{Me})_2$ , 10 min photolysis ( $\lambda_{\text{max}} = 450 \pm 35$  nm) minus 10 min photolysis ( $\lambda_{\text{max}} = 500 \pm 35$  nm), (b)  $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2$ , 10 min photolysis ( $350 \text{ nm} < \lambda_{\text{max}} < 400 \text{ nm}$ ) minus starting spectrum, and (c)  $\text{Os}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2$ , 10 min photolysis ( $300 \text{ nm} < \lambda_{\text{max}} < 400 \text{ nm}$ ) minus starting spectrum in PVC. X corresponds to traces of  $\text{Os}(\text{CO})_3\text{Cl}_2(\text{PPh}_3)_2$  in the photolysis sample.

dissociation would appear to rule out any intersystem crossing to a triplet excited state prior to CO-loss. It was suggested that the  $^1\text{MLCT}$  or  $^1\text{XLCT}$  excited states become dissociative through a strongly avoided crossing with a higher lying LF state. Similar excited state behaviors have been observed for  $\text{Cr}(\text{CO})_4(\text{bipy})$  [18],  $\text{Mn}(\text{CO})_3\text{H}(\text{diimine})$  [19],  $\text{Mn}(\text{CO})_3\text{X}(\text{diimine})$  [20],  $\text{Mn}(\text{CO})_3\text{-Me}(\text{diimine})$  [21].

In order to further define the CO-loss intermediates in these processes we have undertaken an examination of the photochemistry of a series of  $\text{Fe}(\text{CO})_2\text{Br}_2\text{L}_2$ ,  $\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}_2$ , where  $\text{L} = \text{PMe}_3$ ,  $\text{PBu}_3$ ,  $\text{PPh}_2\text{Me}$  and  $\text{PPh}_3$ , and  $\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}$ , where  $\text{L} = \text{bipy}$ ,  $\text{CH}_2(\text{Me}_2\text{Pz})_2$ ,  $\text{CH}_2(\text{MeImid})_2$  and  $\text{TMEDA}$ , compounds in frozen matrices. The matrix photolysis of  $\text{Os}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2$  has also been examined. Additionally, we have carried out bromide abstraction studies on  $\text{Fe}(\text{CO})_2\text{Br}_2\text{L}_2$  derivatives. DFT calculations for isomers of  $\text{Fe}(\text{CO})_2\text{Cl}_2(\text{PMe}_3)_2$  are reported.

## 2. Results and discussion

### 2.1. $\text{M}(\text{CO})_2\text{X}_2\text{L}_2$ photochemistry

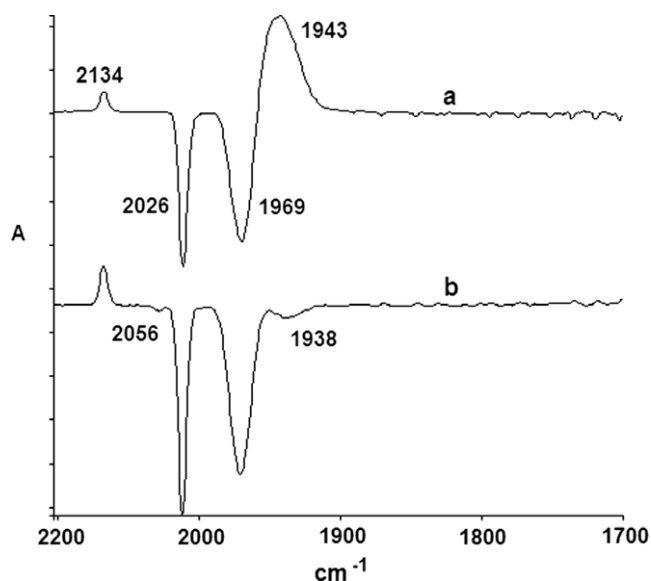
Phosphine derivatives of the form  $\text{M}(\text{CO})_2\text{X}_2\text{L}_2$  were readily prepared by reaction of phosphine ligands with an appropriate metal carbonyl halide using literature procedures. Solubility limitations necessitated the use of PVC films for the *cis, cis, trans*- $\text{M}(\text{CO})_2\text{X}_2(\text{PPh}_3)_2$  series and for the isomers of  $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PMe}_3)_2$ . Iron and ruthenium derivatives of tributylphosphine were soluble

in Nujol so photochemical studies were also carried out in that medium. Photolysis of a set of compounds, *cis, cis, trans*- $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PPh}_2\text{Me})_2$  and *cis, cis, trans*- $\text{M}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2$ ,  $\text{M} = \text{Ru}$  and  $\text{Os}$ , in PVC, Fig. 1, resulted in bleaching of the bands of the carbonyl compounds and growth of two new bands for each compound. The bands at  $2134 \text{ cm}^{-1}$  are characteristic of carbon monoxide in the PVC matrix, while the broad new bands at lower energy are typical of a CO-loss species.

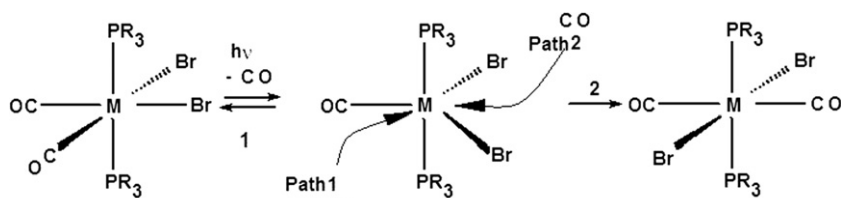
Barnard et al. have suggested that the rearrangement from the *cis, cis, trans* isomer to the all-*trans* isomer in the ruthenium series proceeds via a trigonal bipyramidal, 5-coordinate intermediate, Scheme 1, that can capture CO to either reform the *cis, cis, trans* isomer, or form the all-*trans* isomer. Rest has presented evidence for a trigonal bipyramidal intermediate in the photolysis of  $\text{Mn}(\text{CO})_5\text{Br}$  [22]. In agreement with these workers, we assign the low frequency carbonyl bands to trigonal bipyramidal species,  $\text{M}(\text{CO})\text{X}_2\text{L}_2$ .

Visible photolysis of  $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PBu}_3)_2$  in PVC, Fig. 2a, yields an analogous CO-loss species. UV irradiation of this sample, Fig. 2b, results in CO-loss from both the dicarbonyl precursor and the monocarbonyl photoproduct. The presumed unseen UV photoproduct is presumed to be the 14 electron,  $\text{FeBr}_2(\text{PBu}_3)_2$ .

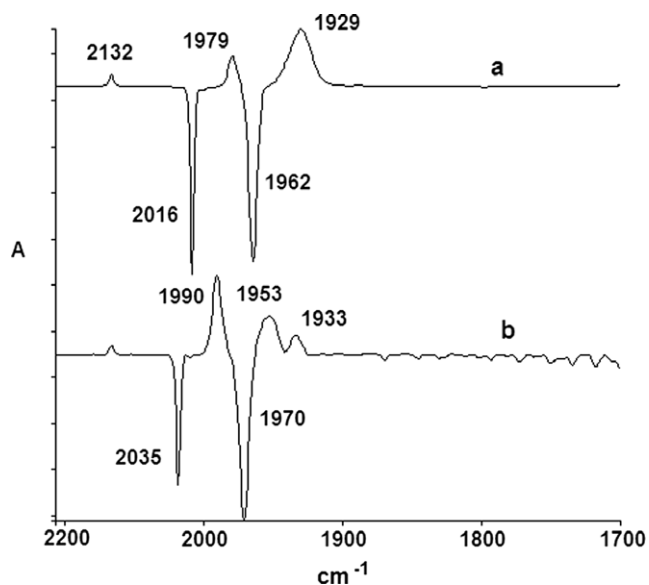
Photolysis of the  $\text{PBu}_3$  derivatives of iron and ruthenium in Nujol, Fig. 3, parallels the PVC results but also gives rise to new photoproducts with carbonyl bands at  $1979$  and  $1990 \text{ cm}^{-1}$ , respectively. The latter is consistent with the carbonyl stretching frequency of all-*trans*- $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PBu}_3)_2$  reported by Nicholson [23] and it is reasonable that the new iron carbonyl band also corresponds to the all-*trans* isomer. The ruthenium compound also gives rise two bands at  $1953$  and  $1933 \text{ cm}^{-1}$  in the region we have



**Fig. 2.** Difference spectra of the photolysis of  $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PBu}_3)_2$  in PVC: (a)  $\lambda_{\text{irr}} = 500 \pm 35$  nm minus  $\lambda_{\text{irr}} > 600$  nm, (b)  $350 \text{ nm} < \lambda_{\text{irr}} < 400 \text{ nm}$  minus  $\lambda_{\text{irr}} = 400 \pm 35$  nm.

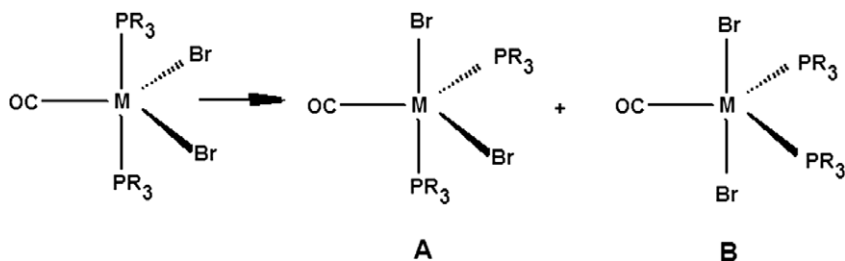


**Scheme 1.** CO lost from  $\text{M}(\text{CO})_2(\text{PR}_3)_2\text{Br}_2$  upon photolysis may be recaptured by the trigonal bipyramidal intermediate along two pathways yielding *cis* and *trans* isomers.

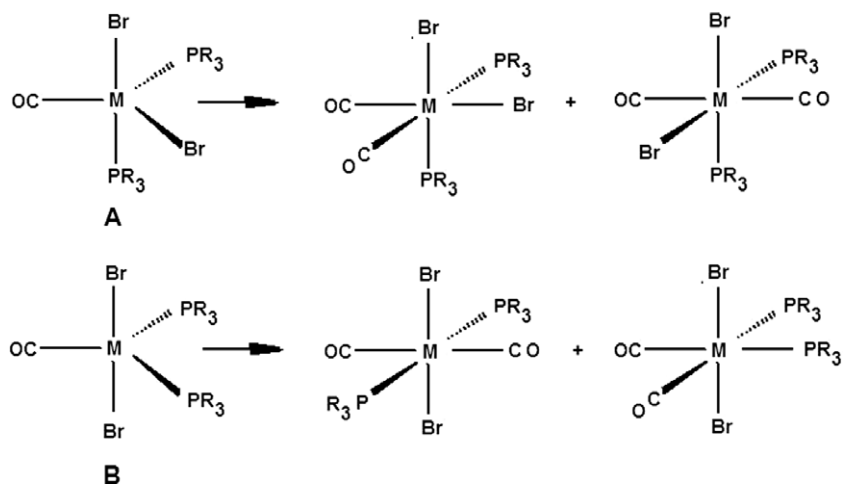


**Fig. 3.** Difference spectra of the photolysis of (a) *cis, cis, trans*-Fe(CO)<sub>2</sub>Br<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub> ( $\lambda_{\text{irr}} = 400 \text{ nm} \pm 35 \text{ nm}$  minus  $\lambda_{\text{irr}} > 600 \text{ nm}$ ) and (b) *cis, cis, trans*-Ru(CO)<sub>2</sub>Cl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub> ( $250 \text{ nm} < \lambda_{\text{irr}} < 400 \text{ nm}$  minus  $\lambda_{\text{irr}} < 400 \text{ nm}$ ) in Nujol.

assigned to CO-loss species. The larger 1953 cm<sup>-1</sup> band is most likely to correspond to a 5-coordinate, Ru(CO)Cl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub> photo-product in which the phosphine groups are in the axial positions. Rearrangement of this species by a Berry-like pseudorotation could exchange a phosphine and chloride ligands to yield the two additional isomers, A and B, shown in Scheme 2.



**Scheme 2.** Possible isomers arising from the rearrangement of the axial-PBu<sub>3</sub> intermediate.

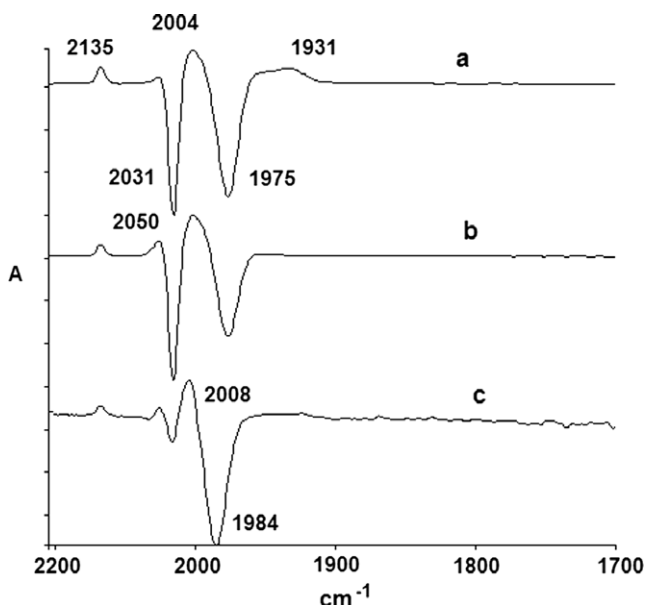


**Scheme 3.** CO recapture products of isomers A and B.

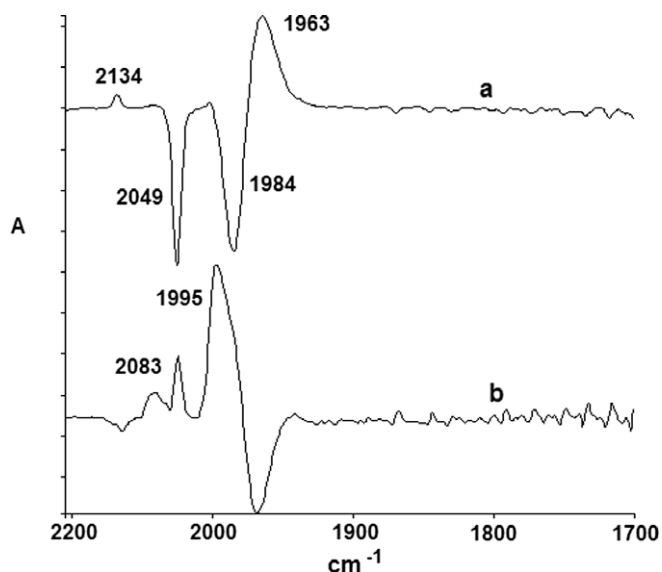
Barnard et al. have demonstrated that all-*cis* isomers are formed upon heating of the photochemically produced all-*trans* derivatives. CO was shown to inhibit the isomerization of all-*trans* to all-*cis*. In Scheme 1 we assume that CO recapture by the trigonal bipyramidal intermediate occurs by attack in the trigonal plane. If we apply the same argument to isomers A and B, we can see in Scheme 3 that isomer A can give rise to all-*cis* and the unobserved *trans, cis, cis*-Ru(CO)<sub>2</sub>Cl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub> isomers, while isomer B gives rise to an all-*trans* isomer and an unobserved *cis, trans, cis*-Ru(CO)<sub>2</sub>Cl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>. Based on the results of the solution studies we propose that the CO-loss species with the band at 1933 cm<sup>-1</sup> corresponds to isomer A.

*cis, cis, trans*-Fe(CO)<sub>2</sub>Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> may be readily transformed into its all-*trans* isomer by exposure to visible light. We were curious to compare the photochemical behavior of these two isomers and so examined their photolyses in PVC matrices. Visible photolysis of the *cis, cis, trans* isomer at wavelengths below 450 nm, Fig. 4a, resulted in CO-loss as evidenced by the free CO band at 2135 cm<sup>-1</sup> and by the broad band of the CO-loss species at 1931 cm<sup>-1</sup>. In addition, bands at 2050 and 2004 cm<sup>-1</sup> were also observed. Continued photolysis into the UV yielded little more of the lower frequency CO-loss species, but further increased the size of the two higher frequency bands. Not surprisingly, the all-*trans* isomer is unaffected by visible photolysis. Photolysis in the UV results in CO loss and the appearance of two bands that appear to correspond to the same species generated by the *cis, cis, trans* isomer. A shallow rise at ca. 1960 cm<sup>-1</sup> is likely attributable to a CO-loss species.

In contrast with the behavior of Fe(CO)<sub>2</sub>Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>, its ruthenium analogue undergoes photolysis in PVC, Fig. 5a, to yield the expected CO-loss product with no new high energy bands. When the matrix was annealed to 140 K, Fig. 5b, and then returned to



**Fig. 4.** Difference spectra of the photolysis of  $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PMe}_3)_2$  in PVC: (a) *cis, cis, trans* isomer,  $\lambda_{\text{irr}} = 450 \pm 35 \text{ nm}$  minus  $\lambda_{\text{irr}} > 600 \text{ nm}$ , (b) *cis, cis, trans* isomer,  $\lambda_{\text{irr}} = 400 \pm 35 \text{ nm}$  minus  $\lambda_{\text{irr}} = 450 \pm 35 \text{ nm}$  and (c) all-*trans* isomer,  $350 \text{ nm} < \lambda_{\text{irr}} < 400 \text{ nm}$  minus  $\lambda_{\text{irr}} = 400 \pm 35 \text{ nm}$ .



**Fig. 5.** Photolysis of  $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PMe}_3)_2$  in PVC: (a) difference spectrum of  $250 \text{ nm} < \lambda_{\text{irr}} < 400 \text{ nm}$  minus  $\lambda_{\text{irr}} > 400 \text{ nm}$  and (b) anneal to 140 K minus  $250 \text{ nm} < \lambda_{\text{irr}} < 400 \text{ nm}$  photolysis.

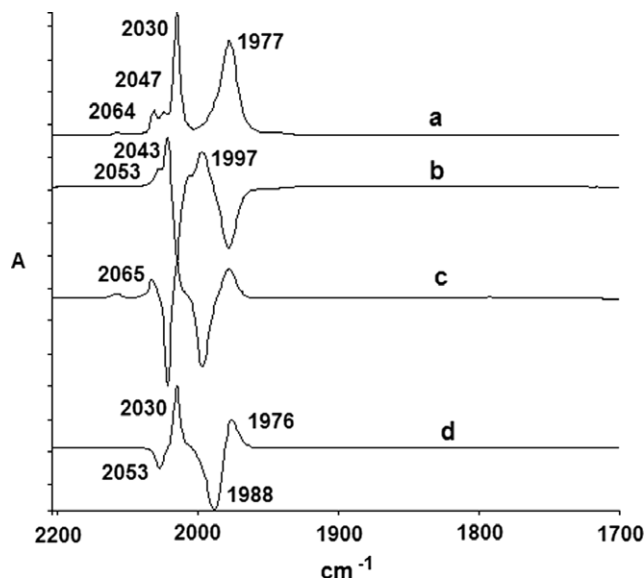
90 K it was found that both the *cis, cis, trans* and all-*trans* isomers were formed.

The high energy carbonyl bands observed in the photolysis of the  $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PMe}_3)_2$  isomers prompted us to examine photochemical alternatives to CO-loss. In their examination of the photochemical isomerization of  $\text{Fe}(\text{CO})_2\text{X}_2\text{L}_2$  derivatives, Pankowski et al. carried out the photolysis of  $\text{Fe}(\text{CO})_2\text{I}_2(\text{PMe}_3)_2$  in the presence of CO and isolated  $[\text{Fe}(\text{CO})_3(\text{PMe}_3)_2]\text{I}$  as a product. In PVC, we reasoned that the matrix might stabilize a halide-loss species. Evans et al. [24] have reported that reaction of  $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2$  with  $\text{AgBF}_4$  in  $\text{CH}_2\text{Cl}_2$  gives isolable products of the form  $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{BF}_4)_2 \cdot \text{X} \cdot \text{CH}_2\text{Cl}_2$  and  $\text{Ru}(\text{CO})_2\text{Cl}(\text{PPh}_3)_2 \cdot \text{X} \cdot 1/2\text{CH}_2\text{Cl}_2$ . We have carried out the corresponding reactions of  $\text{Fe}(\text{CO})_2\text{Br}_2\text{L}_2$ ,

where  $\text{L} = \text{PBu}_3$  and  $\text{PMe}_3$ , with  $\text{AgPF}_6$  and observed immediate precipitation of  $\text{AgBr}$  and formation of new carbonyl bands at 2053, 2043, and 1997  $\text{cm}^{-1}$  that we assign to isomers of the  $\text{Fe}(\text{CO})_2\text{Br}_2\text{L}_2$  cation in solution. Fig. 6a and b illustrate the transformations of the  $\text{PMe}_3$  derivative. The cation is not stable in solution and gradually undergoes disproportionation to reform  $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PMe}_3)_2$  and, we assume, other unseen products, Fig. 6c. Curiously, bromide abstraction from all *trans*  $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PMe}_3)_2$  results in disproportionation to yield the *cis, cis, trans* isomer, Fig. 6d, in the time required to withdraw a sample and record a spectrum. The IR bands of the cationic species formed by the *cis, cis, trans* isomer are in good agreement with the high frequency carbonyl bands observed in the PVC photolysis studies, therefore we conclude that the isomers of  $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PMe}_3)_2$  undergo bromide loss in preference to CO-loss upon UV photolysis.

The differences in behavior of the iron derivatives,  $\text{Fe}(\text{CO})_2\text{Br}_2\text{L}_2$ , where  $\text{L} = \text{PPh}_2\text{Me}$ ,  $\text{PBu}_3$  and  $\text{PMe}_3$  is surprising. The frequencies of the carbonyl bands of these derivatives fall in the order,  $\text{PPh}_2\text{Me} > \text{PMe}_3 > \text{PBu}_3$  predicted by the Tolman electronic parameter. Tolman cone angles for the phosphine ligands are  $\text{PPh}_2\text{Me}$  ( $136^\circ$ )  $>$   $\text{PBu}_3$  ( $132^\circ$ )  $>$   $\text{PMe}_3$  ( $118^\circ$ ) suggesting that is the cone angle of the phosphine and not its electronic character that flips the preferred photochemical manifold from CO to bromide loss. At this point it is not obvious as to why such a fundamental change in photochemistry would be initiated by a small cone angle phosphine.

To assist in understanding the behavior of these compounds, we carried out DFT calculations using the BP86/6-31G\*\* functional and basis set using the SPARTAN 06 computational package. Computed bond length and angle data are presented in Table 1 while computed and experimental carbonyl stretching frequencies are presented in Table 2. The all-*trans* species had no imaginary frequencies, while the *cis, cis, trans* species returned two imaginary frequencies at  $i26$  and  $i33 \text{ cm}^{-1}$ . These frequencies are well within the  $100i \text{ cm}^{-1}$  range proposed by Wang et al. suggestive of an energy minimum identical to, or close to, that arising from the DFT calculation [25]. As such they were not followed. The computed carbonyl frequency values for the *cis, cis, trans* isomer are in remarkably good (and certainly fortuitous) agreement with



**Fig. 6.**  $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PMe}_3)_2$  reaction with  $\text{AgBF}_4$ : (a) *cis, cis, trans*- $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PMe}_3)_2$  in  $\text{CH}_2\text{Cl}_2$  before reaction; (b) after addition of  $\text{AgPF}_6$  minus initial spectrum; (c) reaction mixture after 30 min. minus sample after addition; (d) *trans, trans, trans*- $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PMe}_3)_2$  after  $\text{AgPF}_6$  addition minus initial spectrum.

**Table 1**

Calculated bond lengths (Å) and angles (°) for *cis, cis, trans* and all-*trans*-Fe(CO)<sub>2</sub>Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>

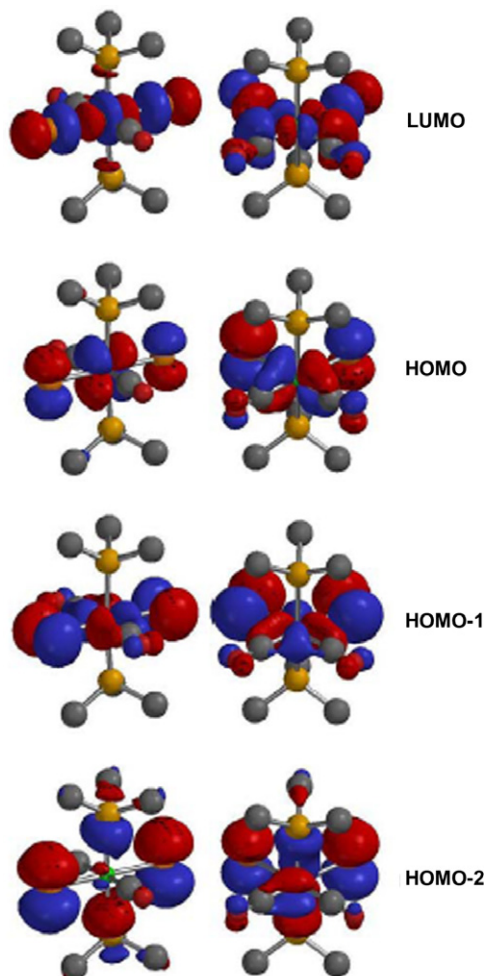
Bond	<i>cis, cis, trans</i>	all- <i>trans</i>
Fe–P	2.284	2.268
Fe–Cl	2.393	2.386
Fe–C	1.730	1.784
C–O	1.172	1.167
Cl–Fe–CO	178.45	
P–Fe–P'	168.41	172.30
Cl–Fe–Cl'	96.69	180.00
OC–Fe–CO	93.75	172.37
P–Fe–CO	93.78	90.26

**Table 2**

Calculated and observed carbonyl stretching frequencies (cm<sup>-1</sup>) for *cis, cis, trans* and all-*trans*-Fe(CO)<sub>2</sub>Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>

<i>cis, cis, trans</i>		all- <i>trans</i>	
Calculated	Observed	Calculated	Observed
2022 (431)	2023	2040 (2.9)	
1974 (497)	1973	1966 (1051)	1987

Calculated intensities in parenthesis.



**Fig. 7.** Kohn–Sham orbitals for all-*trans*-Fe(CO)<sub>2</sub>Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (left) and *cis, cis, trans*-Fe(CO)<sub>2</sub>Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (right).

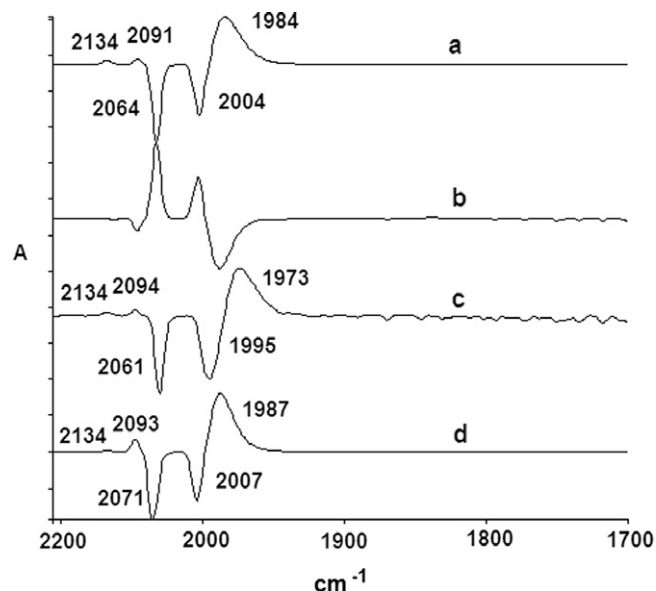
experiment, while the computed value of the asymmetric stretch of the all-*trans* species falls 22 cm<sup>-1</sup> below the observed value.

Both the HOMO and HOMO–1 orbitals of the Fe(CO)<sub>2</sub>Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> isomers, Fig. 7, have Fe–Br π\* character, while the HOMO–2 has significant Br(p) character. The LUMO orbitals are Fe–Br σ\* in character. The LUMO+1 orbitals (not shown) of the all-*trans* isomer have CO π\* character, but this orbital in the *cis, cis, trans* isomer is dominantly Fe(d). We speculate that a HOMO (or HOMO–1) to LUMO excitation for the *cis, cis, trans* isomer results in Fe–Br bond breaking, while the same or similar excitation for other phosphines may evolve down a manifold that results in CO-loss.

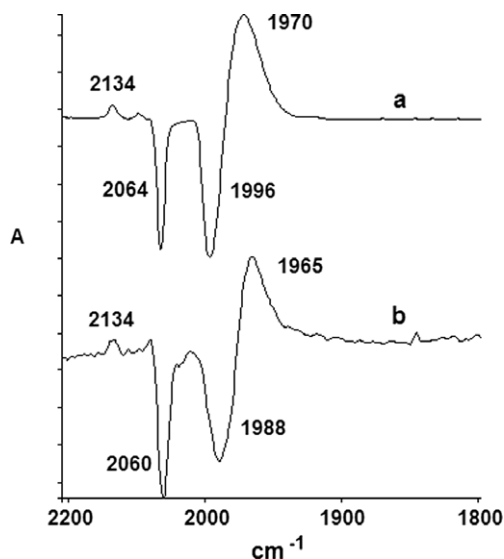
## 2.2. Ru(CO)<sub>2</sub>Cl<sub>2</sub>(κ<sup>2</sup>-L) derivative photochemistry

As noted in Section 1, the photochemistry and photophysics of Ru(CO)<sub>2</sub>Cl<sub>2</sub>(bipy) has been extensively investigated. The lowest electronic absorptions of this class of compounds are either MLCT or XLCT in character as a result of the low lying π\* orbitals of the bipyridine ligand. CO-loss is attributed to <sup>1</sup>MLCT or <sup>1</sup>XLCT excited states that become dissociative through a strongly avoided crossing with a higher lying LF state. We were curious to compare the behavior of the bipyridine derivative with that of CH<sub>2</sub>(Melmid)<sub>2</sub> and CH<sub>2</sub>(Me<sub>2</sub>Pz)<sub>2</sub> recently reported by Messerle et al. [26], and with the TMEDA derivative that has no available π\* orbitals.

Photolysis of *cis, trans*-Ru(CO)<sub>2</sub>Cl<sub>2</sub>(κ<sup>2</sup>-L), where L = bipy, CH<sub>2</sub>(Melmid)<sub>2</sub> and CH<sub>2</sub>(Me<sub>2</sub>Pz)<sub>2</sub>, Fig. 8, results in simple CO-loss. Annealing the matrices reverse this process as illustrated for *cis, trans*-Ru(CO)<sub>2</sub>Cl<sub>2</sub>(κ<sup>2</sup>-bipy), Fig. 8b. Both the *cis, trans* and all *cis* isomers of Ru(CO)<sub>2</sub>Cl<sub>2</sub>(κ<sup>2</sup>-TMEDA) may be isolated and their photolysis was examined in PVC, Fig. 9. CO-loss from these compounds results in the formation of photoproducts with carbonyl bands at 1970 and 1965 cm<sup>-1</sup>, respectively. While the two compounds may yield different 5-coordinate isomers, it is also possible that these are the same species with the slightly lower apparent frequency of the all-*cis* photolysis product arising from an artifact



**Fig. 8.** Photolysis of *cis,trans*-Ru(CO)<sub>2</sub>Cl<sub>2</sub>(κ<sup>2</sup>-L) in PVC. (a) L = bipy, difference spectrum 10 min photolysis λ<sub>irr</sub> = 400 ± 35 nm minus 10 min photolysis λ<sub>irr</sub> = 450 ± 35 nm. (b) L = bipy, difference spectrum, 10 min anneal minus 10 min photolysis 350 nm < λ<sub>irr</sub> < 400 nm. (c) L = CH<sub>2</sub>(Melmid)<sub>2</sub>, difference spectrum 10 min photolysis 350 nm < λ<sub>irr</sub> < 400 nm minus 10 min photolysis λ<sub>irr</sub> > 400 nm. (d) L = CH<sub>2</sub>(Pz)<sub>2</sub>, difference spectrum 10 min photolysis 350 nm < λ<sub>irr</sub> < 400 nm minus 10 min photolysis λ<sub>irr</sub> > 400 nm.



**Fig. 9.** Difference spectrum of  $\text{Ru}(\text{CO})_2\text{Cl}_2(\kappa^2\text{-TMEDA})$  isomers in PVC at ca. 90 K. (a) *cis, trans* isomer, 10 min photolysis 350 nm <  $\lambda_{\text{irr}} < 400$  nm minus 10 min photolysis  $\lambda_{\text{irr}} > 400$  nm. (b) *cis, cis* isomer, 10 min photolysis 350 nm <  $\lambda_{\text{irr}} < 400$  nm minus 10 min photolysis  $\lambda_{\text{irr}} > 400$  nm.

of subtraction of the lower frequency carbonyl band from the photoproduct bands.

### 3. Experimental

*trans*  $\text{Cl}$ ,  $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{bipy})$  [27],  $\text{Ru}(\text{CO})_2\text{Cl}_2[\text{P}(n\text{-Bu})_3]_2$  [28],  $\text{Ru}(\text{CO})_2\text{Cl}_2(\kappa^2\text{-L})$ , where  $\text{L} = \text{CH}_2(\text{Me}_2\text{Pz})_2$  and  $\text{CH}_2(\text{Melmid})_2$  [25],  $\text{Fe}(\text{CO})_2\text{Br}_2\text{L}_2$ , where  $\text{L} = \text{PPH}_2\text{Me}$  and  $\text{PBu}_3$  [29], *cis, cis, trans* and *all-trans* isomers of  $\text{Fe}(\text{CO})_2\text{Br}_2(\text{PMe}_3)_2$  [7],  $\text{Os}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2$  [30], *cis, cis*  $\text{Ru}(\text{CO})_2\text{Cl}_2(\kappa^2\text{-TMEDA})$  [31], and *cis, trans*  $\text{Ru}(\text{CO})_2\text{Cl}_2(\kappa^2\text{-TMEDA})$  [32] were prepared by literature methods. Matrix photochemical methods have previously been reported [33].

### Acknowledgements

We thank the Research Corporation for their support which permitted the purchase of the FT-IR spectrometer used in these studies. This research was generously supported by the National Science Foundation, CHE-0315226.

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