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# Unusual Structure and Reactivity of the Photogenerated Intermediate $Cp^*Cr(\mu\text{-}CO)_3CrCp^*$ ($Cp^* = \eta^5\text{-}C_5Me_5$)

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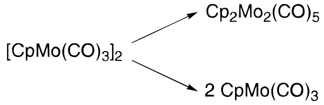
Employing time-resolved IR spectroscopy, we have demonstrated that, following photolysis of $[Cp^*Cr(CO)_2]_2$ (**1**) in *n*-heptane, the only initial photoproduct is the triply bridged CO-loss intermediate $Cp^*Cr(\mu\text{-}CO)_3CrCp^*$ (**4**). *Two* bridging $\nu$(CO) bands are observed, resulting from the splitting of the e′ mode of **4**, which leads to the conclusion that the CO bridging groups are asymmetric. The rate of the back reaction of **4** with CO has been measured ($k_2 = 5.2\ (\pm 0.5) \times 10^7\ M^{-1}\ s^{-1}$), and this is 1000 times faster than the rate of the analogous back reaction of CO with $CpFe(\mu\text{-}CO)_3FeCp$. Moreover, unlike many CO-loss intermediates, there is no reaction of **4** with $PPh_3$. The rate of reaction of **4** with THF, to produce $Cp^*_2Cr_2(CO)_3(THF)$ (**6**), has been estimated ($k_2 = 1.6\ (\pm 0.2) \times 10^8\ M^{-1}\ s^{-1}$).

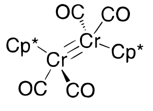
## Introduction

There has been much interest in the photochemistry of transition metal carbonyl dimers.[1−3] There are usually two main primary mechanisms,[4] loss of CO and metal−metal bond fission. For example, the primary photochemical events[5] of $[CpMo(CO)_3]_2$, are:

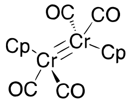


In most cases, shorter wavelength photolysis favors the CO-loss pathway. The identification of the intermediates in metal dimer photochemistry has relied on room temperature flash photolysis, with either visible or infrared detection, and on low temperature matrix isolation.[1,2]

There have been relatively few studies of the photochemistry of the group VI tetracarbonyl dimers, $[CpM(CO)_2]_2$, particularly $[CpCr(CO)_2]_2$. The compounds $[Cp^*Cr(CO)_2]_2$ (**1**) and $[CpCr(CO)_2]_2$ (**2**) ($Cp^* = \eta^5\text{-}C_5Me_5$; $Cp = \eta^5\text{-}C_5H_5$) have interesting structures,[6,7] illustrated schematically:



**1**

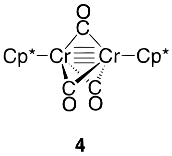


**2**

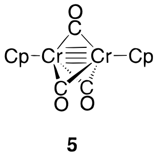
The Cp*−Cr−Cr and Cp−Cr−Cr angles are, respectively, 159° and 162°, and the CO groups, although formally terminal, are bent over the $Cr\equiv Cr$ bond. We shall return to this point later.

In 1981, Robbins and Wrighton[8] described the photochemistry of **1**, **2**, and the mixed species $CpCp^*Cr_2(CO)_4$ (**3**). They concluded that the photochemistry proceeds via loss of a CO group: photolysis in the presence of excess CO suppresses the photochemistry and, in the presence of $^{13}CO$, photolysis of **1** and **2** leads to exchange of $^{12}CO$ by $^{13}CO$, presumably via the intermediate $Cp^*_2Cr_2(CO)_3$ **4** or $Cp_2Cr_2(CO)_3$ **5**. Interestingly, attempts to substitute CO by entering ligands such as ethylene, $PPh_3$, or $P(OMe)_3$ only led to decomposition, although with $PF_3$, uncharacterized substitution products were obtained. Photolysis of **1** and **2** together did not produce any evidence for **3**, and on this and other evidence, it was concluded that photolysis does not lead to the generation of $15e^-$ fragments, $Cp^*Cr(CO)_2$ or $CpCr(CO)_2$, via Cr−Cr bond fission. It was suggested that Cr−Cr fission does not occur because the formally triple $Cr\equiv Cr$ bond is too strong.

Hooker and Rest[9] showed that photolysis of **1** and **2** in low temperature PVC matrices led to changes in the $\nu$(CO) infrared spectrum. Loss of parent $\nu$(CO) bands of either **1** or **2** was accompanied by production of a single broad band in the CO-bridging region, and, by analogy with the well known fragment $Cp_2Fe_2(\mu\text{-}CO)_3$,[10] it was concluded that the species produced were the intermediates **4** or **5** with the structures:



**4**



**5**

The local symmetry of the CO groups is $D_{3h}$, giving rise to a single $\nu$(CO) band of e′ symmetry. It was also

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.

(1) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187−218.

(2) Turner, J. J.; Poliakoff, M.; Healy, M. A. *J. Pure Appl. Chem.* **1989**, *61*, 787−794.

(3) Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217−240.

(4) In this paper we concentrate on those intermediates which lead to real chemical change; hence we shall ignore the fascinating species that can occur on fs and ps timescales.

(5) Peters, J.; George, M. W.; Turner, J. J. *Organometallics* **1995**, *14*, 1503−1506, and references therein.

(6) Potenza, J.; Giordano, P.; Mastropaolo, D.; Efraty, A. *Inorg. Chem.* **1974**, *13*, 2540−2544.

(7) Curtis, M. D.; Butler, W. M. *J. Organomet. Chem.* **1978**, *155*, 131−145.

(8) Robbins, J. L.; Wrighton, M. S. *Inorg. Chem.* **1981**, *20*, 1133−1139.

(9) Hooker, R. H.; Rest A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 1221−1229.

(10) Hooker, R. H.; Mahmoud, K. A.; Rest A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1022−1024.

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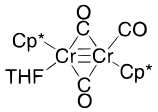
**Table 1: Selected Frequencies and FWHM (in Parentheses), in cm$^{-1}$, of the Chromium Dimer Complexes**

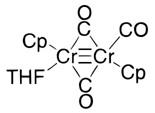
| species | $\nu$(CO)/cm$^{-1}$ PVC matrix[a] | RT *n*-heptane[b] |
|---|---|---|
| $[Cp^*Cr(CO)_2]_2$ | 1871 (≈20) | 1877 (~7.0) |
| | 1845 (≈20) | 1857 (~6.5) |
| $Cp^*_2Cr_2(\mu-CO)_3$ | 1788 (≈22) | 1796 (~7) |
| | | 1785 (~9) |
| $Cp^*_2Cr_2(CO)_3(THF)$ | 1879 | 1881 |
| | 1767 | 1774 |
| | 1728 | ~1740 |

[a] Reference 9. [b] This work.

shown that on warming up a PVC matrix, cast from THF solution, the $\nu$(CO) bands due to **4** or **5** disappeared and new bands appeared which were assigned to $Cp^*_2Cr_2(CO)_3(THF)$ (**6**) or $Cp_2Cr_2(CO)_3(THF)$ (**7**) with the possible structures:



**6**



**7**

On further warming the PVC matrix, the bands due to the THF complex disappeared, and the parents **1** or **2** were reformed as the photoejected CO, still trapped in the matrix, combined with the fragment.

Although the matrix technique is invaluable for the identification of intermediates, the nature of the experiment precludes the obtaining of kinetic data. On the other hand, the $\nu$(CO) data from matrix experiments often assist in the study of intermediates at room temperature by very fast time-resolved infrared spectroscopy (TRIR).[2] We have examined the photochemistry of **1** in *n*-heptane solution by TRIR and identified the intermediate **4**. In the bridging $\nu$(CO) region there are in fact *two* closely spaced bands; we assign these to the ($\mu$-CO)$_3$ group in which the local symmetry is lowered ($C_{2v}$ or $C_s$, rather than $D_{3h}$). We have also monitored the reaction of **4** with CO and with THF and have obtained appropriate kinetic data. The reaction of **4** with CO is some three orders of magnitude faster than the corresponding reaction of $Cp_2Fe_2(\mu\text{-}CO)_3$.[11]

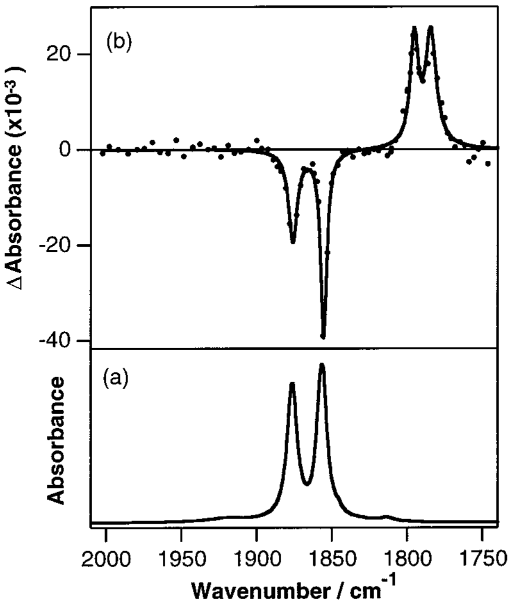


**Figure 1.** FTIR spectrum (Perkin-Elmer System 2000 spectrometer) of $[Cp^*Cr(CO)_2]_2$ in *n*-heptane ($5 \times 10^{-4}$ M). TRIR spectra of $[Cp^*Cr(CO)_2]_2$ in *n*-heptane ($5 \times 10^{-4}$ M), in the presence of 2 atm of CO, obtained 200 ns after UV (355 nm) excitation. Data points plotted downwards indicate loss of parent; data points plotted upwards indicate generation of new species. The solid line is a multiple Lorentzian fit to the data.

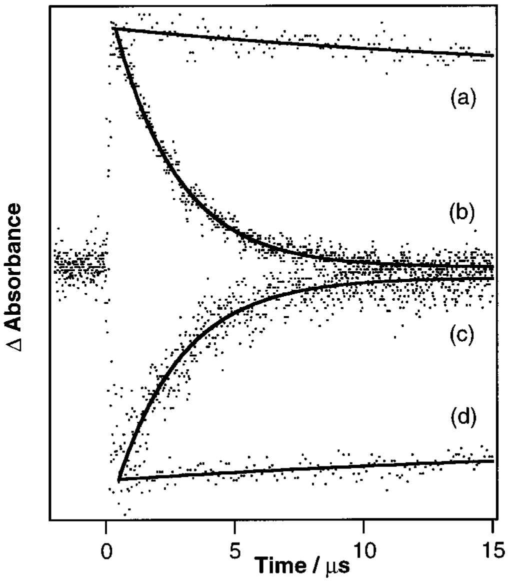


**Figure 2.** Time-resolved kinetic traces obtained following UV excitation of $[Cp^*Cr(CO)_2]_2$ in *n*-heptane ($5 \times 10^{-4}$ M) at the intermediate absorption, 1794 cm$^{-1}$ (traces a and b) and at the parent absorption 1853 cm$^{-1}$ (c and d) in the presence of 2 atm of Ar (a and d) and 0.5 atm of CO (b and c). The solid lines are exponential fits through the data points. The traces have been autoscaled.

## Results

Figure 1a shows the $\nu$(CO) FTIR spectrum of $[Cp^*Cr(CO)_2]_2$ **1** in *n*-heptane at room temperature. The two bands are assigned to the two a$_u$ modes resulting from the $C_i$ symmetry of **1** [$C_i$ symmetry in solid;[6] conceivably $C_{2h}$ in solution with a$_u$ and b$_u$ bands]. Figure 1b shows the time-resolved infrared (TRIR) spectrum obtained 200 ns after UV (355 nm) photolysis of **1** in *n*-heptane in the presence of 2 atm of CO. It is clear that photolysis leads to loss of parent and generation of two new spectral features at 1796 and 1785 cm$^{-1}$ (Table 1). At longer timescales these two bands decay away at the same rate, the parent bands reform, and no other spectral features are seen. Figure 2 shows the decay of the 1796 cm$^{-1}$ band and the corresponding growth of the parent band at 1853 cm$^{-1}$, under two different concentrations of CO. The rate increases with CO concentration. Under 1.75 atm of CO the kinetics are pseudo first order. The rate constant for loss of the 1796 cm$^{-1}$ band, $k_{obs} = 1.4\ (\pm 0.2) \times 10^6$ s$^{-1}$, is equal to the recovery of parent, $k_{obs} = 1.6\ (\pm 0.2) \times 10^6$ s$^{-1}$. Identical results, within experimental error, were obtained for the 1785 cm$^{-1}$ band. Three main conclusions can be drawn:

(i) the bands at 1796 and 1785 cm$^{-1}$ belong to the same species;

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(11) Dixon, A. J.; George, M. W.; Hughes, C.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1992**, *114*, 1719–1729 and references therein.

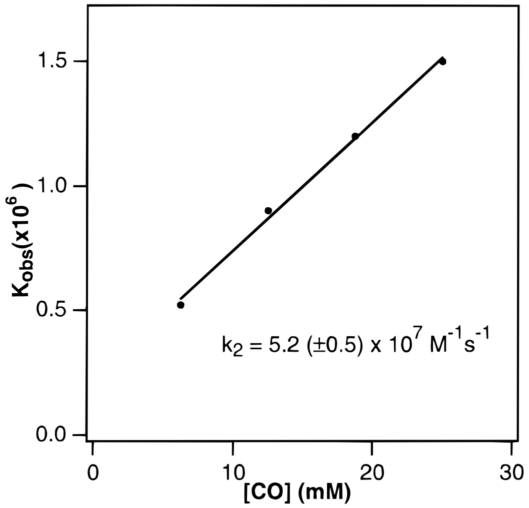

**Figure 3.** Plot of the observed decay rate ($s^{-1}$) of the 1796 $cm^{-1}$ band versus CO concentration.

(ii) this species is a CO-loss intermediate;

(iii) the 1796/1785 pair are in the same region as the broad 1788 $cm^{-1}$ band assigned in a PVC matrix to $Cp^*{}_2Cr_2(\mu\text{-}CO)_3$ (Table 1).[9]

Thus the 1796/1785 $cm^{-1}$ pair are assigned to $Cp^*{}_2Cr_2(\mu\text{-}CO)_3$ **4** in room temperature solution. The surprise is that, rather than a single band, there are two bands separated by 11 $cm^{-1}$. If the local symmetry of the ($\mu$-$CO_3$) group is lowered from $D_{3h}$ to $C_{2v}$ symmetry then the degeneracy of the e′ mode is lifted and we expect the $\nu$(CO) band to split into two bands of approximately equal intensity, and with symmetry classification $a_1/b_1$. The high frequency mode which has $a_1'$ symmetry under $D_{3h}$ symmetry, and which is inactive in the infrared, becomes $a_1$ under $C_{2v}$ and infrared active. However, since the splitting of the e′ mode is only 11 $cm^{-1}$, it is likely that the distortion is small and hence the new $a_1$ band is expected to be very weak and not observed in our experiments. This lifting of the e′ mode degeneracy is the most probable explanation of the splitting; we take up the question as to why in Discussion.

As stated above, TRIR can provide kinetic data. Figure 3 shows a plot of $k_{obs}$ for the decay of the 1796 $cm^{-1}$ band of **4** under different pressures of CO. The rate is linear with [CO] and, knowing the solubility of CO in *n*-heptane,[12] allows the calculation of the second order rate constant of **4** with CO, $k_2 = 5.2\ (\pm 0.5) \times 10^7$ $M^{-1}\ s^{-1}$. The rate for the reaction of the similar intermediate species $Cp_2Fe_2(\mu\text{-}CO)_3$ with CO is ~1000 times slower[11] ($6 \times 10^4\ M^{-1}\ s^{-1}$) and the more exact analogy, $Cp^*{}_2Fe_2(\mu\text{-}CO)_3$, can even be isolated and is sufficiently stable for a crystal structure determination![13] This difference probably arises because of the different spin states of the two species, and we return to this point in Discussion.

We have also looked for evidence of the reaction of **4** with $PPh_3$. Following flash photolysis of **1** in $PPh_3$-doped *n*-heptane, TRIR showed the generation of **4**, but there was no evidence that this reacted with $PPh_3$; it simply reacts with CO and regenerates the parent. This confirms the early preparative photochemical studies.[8]

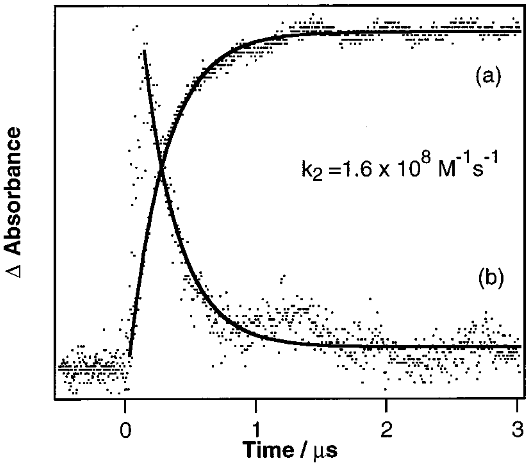

**Figure 4.** Time-resolved kinetic traces recorded at (a) 1745 and (b) 1797 $cm^{-1}$, following UV (355 nm) photolysis of $[Cp^*Cr(CO)_2]_2$ in *n*-heptane ($5 \times 10^{-4}$ M), in the presence of THF (0.025 M). The solid lines are exponential fits through the data points.

However in *n*-heptane doped with THF (0.025 M), flash photolysis generates **4**, which reacts with the THF to yield a species with three $\nu$(CO) bands at 1881, 1774, and ~1740 $cm^{-1}$. In the PVC matrix the species assigned to $Cp^*{}_2Cr_2(CO)_3(THF)$ **6**, has bands at 1879, 1767, and 1728 $cm^{-1}$ (Table 1).[9] Clearly we are observing the same species. The rate of loss of **4**, and grow-in of **6**, both show pseudo first order kinetics. Figure 4 shows that **6** is formed at the same rate that **4** decays, $k_{obs} = 4\ (\pm 0.4) \times 10^6$ and $= 4.5\ (\pm 0.4) \times 10^6\ s^{-1}$, respectively. Thus the second order rate constant for the reaction of **4** with THF can be estimated, $k_2 = 1.6$ $(\pm 0.2) \times 10^8\ M^{-1}\ s^{-1}$. On the timescale of the TRIR experiments, there is no loss of **6**.

## Discussion

**Structure of $Cp^*{}_2Cr_2(\mu\text{-}CO)_3$.** The first question is why does the bridging $\nu$(CO) band appear split in solution but is a single band in the PVC matrix? One possible explanation is that $\nu$(CO) bands in PVC matrices are invariably rather broad, and hence any small splitting can be disguised. It is noteworthy that in the PVC matrix the bridging band has FWHM of ~22 $cm^{-1}$, see Table 1. Given that the two solution bands are separated by only 11 $cm^{-1}$, it is clear that such a splitting would not be observed in the matrix. One way of probing this is to use a matrix environment in which $\nu$(CO) bands are known to be much narrower; the obvious choice is a frozen noble gas matrix. However Hooker and Rest[9] comment that it was not possible to carry out such an experiment because the parent molecule is not sufficiently stable to deposit from the gas phase. An alternative is polyethylene. In such a matrix we find that the bands of **1** are narrower than in PVC (~9 $cm^{-1}$, compared with ~20 $cm^{-1}$); photolysis produces a broad band at 1790 $cm^{-1}$ which does show evidence for splitting.

It is interesting to compare these results with the analogous intermediates, $Cp^*{}_2Fe_2(\mu\text{-}CO)_3$ and $Cp_2Fe_2(\mu\text{-}CO)_3$. We have generated the former by conventional photolysis of $[Cp^*Fe(CO)_2]_2$ in *n*-heptane and measured

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[12] 1 atm CO = $1.25 \times 10^{-2}$ M. Makrancy, J.; Megyery-Balog, K.; Rusz, L.; Patyi, L. *Hung. J. Ind. Chem.* **1976**, *4*, 269–280.

[13] Blaha, J. P.; Bursten, B. E.; Dewan, J. C.; Frankel, R. B.; Randolf, C. L.; Wilson, B. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 4561–4562.

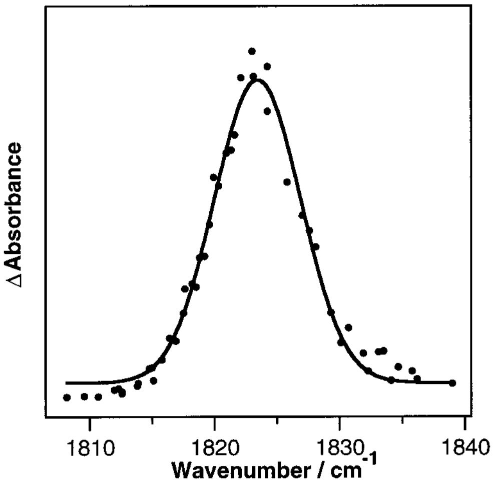

**Figure 5.** TRIR spectrum of the triply bridging band of $CpFe(\mu\text{-}CO)_3FeCp$, obtained 20 μs after UV (355 nm) photolysis of $[CpFe(CO)_2]_2$ in *n*-heptane ($1 \times 10^{-3}$ M), in the presence of 2 atm of argon. The solid line is a Lorentzian fit to the data.

the bandwidth by FTIR (7.0 (±0.5) $cm^{-1}$). We have repeated TRIR measurements on $Cp_2Fe_2(\mu\text{-}CO)_3$, produced by flash photolysis of $[CpFe(CO)_2]_2$ in *n*-heptane, see Figure 5; it can be seen that there is a single band with FWHM of $\sim$8 $cm^{-1}$. It is worth adding that in a $CH_4$ matrix, where the narrowest bands are expected, the FWHM of the bridging band of $Cp_2Fe_2(\mu\text{-}CO)_3$ is *ca.* 5.5 $cm^{-1}$.[10] This evidence therefore demonstrates that for $Cp^*_2Cr_2(\mu\text{-}CO)_3$, the $\nu$(CO) e′ mode is split into two, but in the analogous iron complexes the corresponding mode gives a single band with fairly narrow halfwidth.

It is interesting to speculate what might be the connection between the band splitting and any structural effect. The simplest approach is to use the relationship deduced from a comparison of crystallographic data and CO force constants:

$$r_{CO} = 1.647 - 0.184 \ln k_{CO}$$

where $r_{CO}$ is the CO bond length in Å, and $k_{CO}$ is the energy-factored CO force constant.[14] The crystal structure of $Cp^*_2Fe_2(\mu\text{-}CO)_3$ has been previously determined.[13] Although all values of $r_{CO}$ are the same, within the ESD's quoted, a difference of less than 0.25% in the bond lengths, well within the ESD's, would result in a splitting of 10 $cm^{-1}$ of the e′ mode. Since no such splitting is observed for this compound, we can say that the CO bond lengths are the same to within 0.25%. This is an unusual example where infrared provides more sensitive structural data than crystallography!

There is obviously no crystallographic data for $Cp^*_2Cr_2(\mu\text{-}CO)_3$. If we assume that the splitting of 11 $cm^{-1}$ arises from a difference in principal force constants between one CO group ($k_1$) and the other two ($k_2$) (i.e. $C_{2v}$ vibrational symmetry), but that the interaction constants $k_{12}$ and $k_{22}$ are equal, then a difference between $k_1$ and $k_2$ of <1% results in the observed splitting. This implies a CO bond length difference of 0.3%.

There are two possible reasons for the splitting of the $\nu$(CO) e′ mode. The first is that, although the local symmetry of the $(\mu\text{-}CO)_3$ group is three-fold, there is sufficient interaction with the $C_5Me_5$ rings, which have five-fold symmetry, that the effective symmetry is reduced to $C_{2v}$. This effect is not uncommon in organometallic compounds. However this does not occur for the analogous iron compound—why not? One possible explanation lies in the molecular orbital diagrams for the two different sorts of species. Figure 6 shows the MO diagram for $CpFe(\mu\text{-}CO)_3FeCp$, based on the work of Hoffmann and colleagues[15] and of Wrighton and colleagues.[13] For $Cp_2Fe_2(\mu\text{-}CO)_3$, which is a 32-electron species, the orbitals are full up to and including the e′ + e″ set. The e″($\pi^*$) degenerate pair contains only two electrons. As demonstrated experimentally by Wrighton,[13] this makes the analogous $Cp^*_2Fe_2(\mu\text{-}CO)_3$ paramagnetic. $Cp^*_2Cr_2(\mu\text{-}CO)_3$ is a 28-electron species. If two electrons are removed from the antibonding e″ set and two from the next set (e′+e″, $a_2''$, $a_1'$) then, since the latter are almost nonbonding, there will be an overall shortening of the Cr−Cr bond. This will increase the interaction between the Cp* rings and the bridging CO groups.

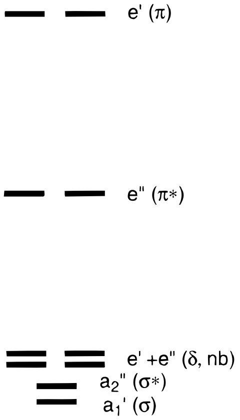

**Figure 6.** Important orbitals from the molecular orbital diagram for $CpFe(\mu\text{-}CO)_3FeCp$, based on reference 13.

An alternative explanation is that, whereas the X-ray structure of $Cp^*_2Fe_2(\mu\text{-}CO)_3$ shows a linear Cp*−Fe−Fe−Cp* arrangement,[13] it is possible that in the analogous Cr compound, the Cp*−Cr−Cr−Cp* arrangement is bent; this would make the $(\mu\text{-}CO)_3$ group have, at best, $C_s$ symmetry, leading to a splitting of the e′ mode into two bands of a′ and a″ symmetry. It is noteworthy that in both **1** and **2** the Cp (orCp*)−Cr−Cr−Cp (orCp*) arrangement is bent, although in the analogous molybdenum compound, $[CpMo(CO)_2]_2$, the corresponding arrangement is linear.[16] Hoffmann and colleagues have shown that for these compounds the energy difference between the linear and bent arrangements is very small.[17] For the triply bridged species, a similar analysis is difficult because as the molecule distorts, the symmetry drops from $D_{3h}$ to $C_s$, and consequently following the orbital energy path is more difficult.

**Kinetics of Reactions of $Cp^*_2Cr_2(\mu\text{-}CO)_3$.** There has been considerable interest in the influence of spin state on the reaction rates of organometallics with different substrates.[18,19b] In classic gas phase studies on $Fe(CO)_4$, which matrix studies showed to have a

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[14] Morrison, S. L.; Turner, J. J. *J. Mol. Struct.* **1994**, *317*, 39−47.

[15] Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219−3224.

[16] Klingler, R. J.; Butler, W. M.; Curtis, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 3535−3536.

[17] Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2576−2585.

triplet ground state,[20] TRIR showed that it reacts quite slowly.[19] $Cp_2Fe_2(\mu\text{-}CO)_3$ is also a triplet and reacts relatively slowly. The fact that **4** reacts so fast with CO compared with the analogous iron complexes suggests that its ground state might be a singlet. This would require that the highest orbital for **4** in the lowest group of 6 orbitals (see Figure 6) is actually $a_2''$ or $a_1'$; if this highest orbital were e′ or e″, then the ground state of **4** would be a triplet.

As mentioned in the introduction, photolysis of **1** and **2** in the presence of $PPh_3$ leads first to the production of **4**, but there is no evidence of reaction of **4** with $PPh_3$; the parent is regenerated. In contrast the iron compounds form substituted products on photolysis with $PPh_3$.[21] The explanation of the difference most probably lies in steric effects.

## Conclusion

We have shown again that TRIR spectroscopy is an excellent probe for the kinetic and structural study of organometallic photointermediates. Upon photolysis $[Cp^*Cr(CO)_2]_2$ undergoes CO-loss only; there is no detectable Cr−Cr bond fission. The photogenerated CO-loss species, $Cp^*Cr(\mu\text{-}CO)_3CrCp^*$, has been shown to have both (i) an unusual structure, asymmetric (*i.e.* non $D_{3h}$) $(\mu\text{-}CO)_3$ bridging carbonyls; and (ii) high reactivity (compared with the Fe analogue) in solution at room temperature. These data necessarily afford a new interpretation of previous matrix isolation data. Furthermore we have shown that under rather special circumstances infrared can provide more sensitive structural data than crystallography!

## Experimental Section

The Nottingham TRIR apparatus has been described in detail elsewhere.[22] Briefly, it consists of a pulsed UV/vis source, a Nd:YAG laser (Quanta-Ray GCR-11; 355 nm, or 532 nm, 7 ns pulse), to initiate photochemical reactions and a cw IR laser, (Mütek IR diode laser; MDS 1100), to monitor the transient IR absorptions. The change in IR transmission at one particular IR frequency is measured following excitation, and IR spectra are built up on a "point-by-point" basis by repeating this measurement at different IR frequencies.

The low temperature matrix apparatus has been previously described elsewhere.[23] Briefly, the polymer matrix experiments use 250 μm LDPE disks, mounted inside a "Low-Temperature, High-Pressure" cell. The cell is fixed to the cold finger of a cryogenic cooling system capable of temperature stabilization of ±0.1 K, with a minimum temperature of 30 K. The vacuum shroud, evacuated by a turbomolecular pump, has two $CaF_2$ windows, aligned with those of the cell. Photolysis is conducted using a medium pressure Hg arc lamp (Philips HPK-125UV), providing broad-band UV ($300 < \lambda < 400$ nm) radiation. IR spectra are recorded at 2 $cm^{-1}$ resolution using a Nicolet 730 spectrometer.

$[Cp^*Cr(CO)_2]_2$ (Strem), $[CpFe(CO)_2]_2$, and $[Cp^*Fe(CO)_2]_2$ (both various sources) were used as supplied. *n*-Heptane (Aldrich, HPLC Grade) was distilled over $CaH_2$ prior to use. THF (Aldrich, Anhydrous 99.9%), Ar, He (Air products), and CO (BOC) were used as supplied.

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