Photochemistry of Some Group 6A and 8 Metal–Metal Bonded Cyclopentadienylcarbonyl Dimers in Poly(vinyl chloride) Films at 12—298 K

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Infrared and electronic spectral evidence is presented which shows that photolysis of the dinuclear complexes $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CO)_2]$, $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_6]$ (M = Mo or W, R = H or Me), and $[Cr_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ in poly(vinyl chloride) (pvc) films at *ca.* 12—77 K produces dissociative CO loss as the primary process. The products are assigned as $[Ni_2(\eta^5\text{-}C_5H_4Me_2)_2(\mu\text{-}CO)]$, $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_5]$ (M = Mo or W; two terminal CO, two semibridging CO, one four-electron bridging CO ligand), and $[Cr_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}CO)_3]$. Annealing the films to 100—200 K resulted in facile reversal of the primary process. Similar reversal was achieved by irradiating into the long wavelength absorptions of the products at 12—77 K. Photolysis of the *cis* and *trans* bridged isomers of $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in pvc films did *not* lead to CO ejection at 12 K but only to bridge opening. Photolysis of *trans*-$[Ru_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$ afforded neither CO loss nor even bridge opening, probably due to steric factors. Photolysis of the complexes $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_6]$ (M = Mo or W, R = H or Me) and $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ (M = Fe or Ru, R = H or Me) in pvc films at 298 K afforded the mononuclear complexes $[M(\eta^5\text{-}C_5R_5)(CO)_3Cl]$ and $[Ru(\eta^5\text{-}C_5R_5)(CO)_2Cl]$ arising from abstraction of Cl from the films, *cf.* the photoreactions observed in chlorocarbon solvents. The mechanisms of the photochemical reactions in pvc films are discussed in relation to solution photochemical reactions.

A variety of photoreactions of dinuclear Group 6A and 8 metal carbonyl complexes have been observed in solution.[1–8] For example, photolysis of the complexes $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ (M = Cr, Mo, or W) in pure hydrocarbon solvents[1] leads to the formation of the M≡M triple bonded dimers $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ whilst irradiation of the parent dimers (M = Mo or W) in chlorocarbon solvents[2] leads to the mononuclear products $[M(\eta^5\text{-}C_5H_5)(CO)_3Cl]$. The complexes $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ (M = Mo or W) undergo photosubstitution of CO by donor ligands L (*e.g.* PPh_3) in solution[3a,b] to form products of the type $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_5L]$ and $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4L_2]$. The photochemistry of the parent dimers has been rationalised[5] in terms of a primary photoprocess in which homolytic cleavage of the M–M single bond occurs, *cf.* equation (1).

$$[M_2(\eta^5\text{-}C_5H_5)_2(CO)_6] \xrightarrow[\text{near u.v.–visible}]{h\nu} 2[M(\eta^5\text{-}C_5H_5)(CO)_3]^{\bullet} \quad (1)$$

The photoconversion of the CO-bridged dimers $[M'_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (M′ = Fe or Ru) into the $[M'(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ complexes in CCl_4 solutions[6,7] and the photoreactions of the iron complex with donor ligands[3c] to yield substitution products, *e.g.* $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2\{P(OMe)_3\}_2]$, have been proposed to proceed *via* radical pathways [equation (2)].[7] There is also some support for a mechanism involving a mono-CO-bridged intermediate $[(OC)_2(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)Fe(\eta^5\text{-}C_5H_5)(CO)]$.[8]

$$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4] \xrightarrow[\text{near u.v.–visible}]{h\nu} 2[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^{\bullet} \quad (2)$$

Flash photolysis studies of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ and $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in solution[9a,b] provided kinetic evidence for both CO dissociation pathways [equations (3) and (4)] and radical pathways [equations (1) and (2)].

$$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4] \xrightarrow[\text{near u.v.–visible}]{h\nu} [Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3] + CO \quad (3)$$

$$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6] \xrightarrow[\text{near u.v.–visible}]{h\nu} [Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5] + CO \quad (4)$$

Infrared evidence in support of the CO dissociation pathway was afforded by the photolysis of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in poly(vinyl chloride) (pvc) films at 12—77 K.[10] The products were CO and triply CO-bridged dimer $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_3]$. The dimer was subsequently observed in hydrocarbon glasses[11] and was found to have an electronic spectrum identical with that of the CO-loss transient detected in the u.v.–visible flash photolysis study.[9a] Following the development of a laser i.r. flash photolysis technique both $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_3]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^{\bullet}$ were detected in solution at ambient temperatures.[12]

This paper describes a study of the photochemistry of the dimers $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ (M = Cr, Mo, or W; R = H or Me), $[M'_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ (M′ = Cr or Ru, R = H or Me), and $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CO)_2]$ in pvc films at 12—298 K. The results are discussed in relation to the mechanisms proposed for the photoreactions of the dimers observed in solution. A preliminary account of the results for the dimers where M = Mo or W has been published elsewhere.[13]

Experimental

Equipment for low-temperature studies, spectrometers, the photolysis lamp, and casting of pvc films has been described elsewhere.[14] The complexes were gifts from Dr. H. G. Alt, Dr. J. Evans, and Professor J. L. Spencer and were used without further purification.

Wavelength-selective photolyses were achieved as follows: filter A, λ > 320 nm, soda glass disc (thickness 3 mm); filter B, λ > 350 nm, Corning colour filter, CS 3850 (thickness 3 mm); filter C, λ > 400 nm, Pyrex glass disc (thickness 2 mm) +

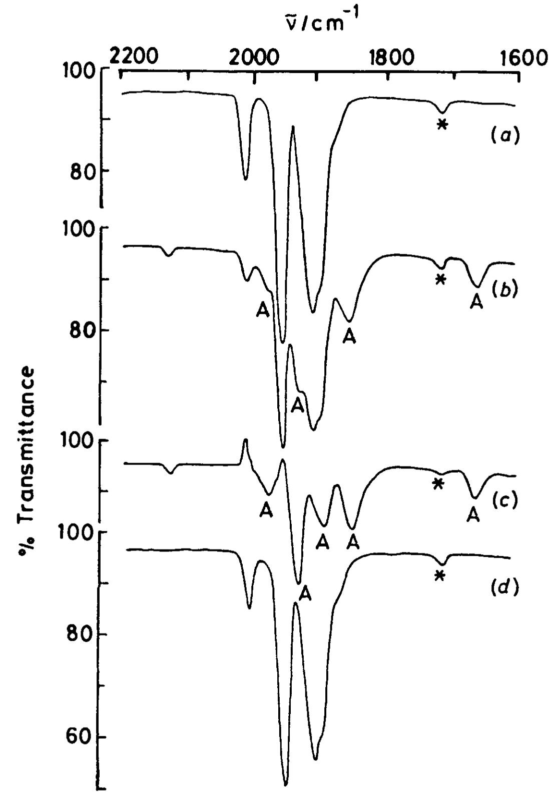
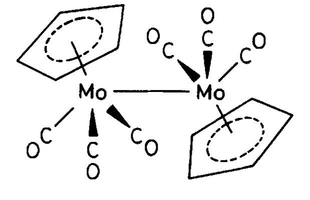


Figure 1. Infrared spectra from an experiment with $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in a pvc film (cast from a thf solution) at 12 K: (*a*) before irradiation; (*b*) after 15 min of irradiation ($\lambda > 400$ nm); (*c*) spectral subtraction, (*b*) − *N*(*a*), where *N* is a scaling factor; (*d*) after warming film to *ca.* 180 K. Bands marked A are for the photoproduct (see text) and that marked * is for ketone groups in pvc

quartz gas cell (pathlength 25 mm) containing Cl_2 gas (2 atm, *ca.* 2×10^5 Pa); filter D, 280 < λ 370 nm. Pyrex glass disc (thickness 2 mm + glass cell (pathlength 25 mm) containing Br_2 gas (300 Torr *ca.* 4×10^4 Pa); filter E, 300 < λ < 400 nm, Corning colour filter, CS 7-54 (thickness 3 mm).

Results

(*i*) *Photolysis of* $[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$, $[Mo_2(\eta^5\text{-}C_5R_5)_2(CO)_6]$ (R = H *or* Me) and $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$.— Figure 1(*a*) shows the i.r. spectrum of the complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ at 12 K in a pvc film (4 mg per 500 mg) cast from a tetrahydrofuran (thf) solution (298 K). The spectrum is very similar to that observed for the dimer in polar solvents such as CH_2Cl_2. Three terminal carbonyl stretching bands ($A_u + 2B_u$) are expected for this complex which formally has the centrosymmetric *trans* structure (**1**) (C_{2h} symmetry)[15] shown below.



(**1**)

The spectrum actually shows a broad band at 1 909 cm⁻¹ (resolved into two bands in hydrocarbon solvents) and two other bands at 2 010 and 1 955 cm⁻¹. The highest-energy band is assigned to non-centrosymmetric *gauche* rotamers of the dimer by analogy with the solution spectra obtained previously.[16] The electronic absorption spectrum of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in the film at 12 K is shown in Figure 2(*a*). The spectrum shows an intense band in the near-u.v. region ($\lambda_{max.}$ 380 nm) and a weaker band in the visible region ($\lambda_{max.}$ 510 nm). The former band has been assigned[2] to a $\sigma \longrightarrow \sigma^*$ transition localised on the Mo–Mo single bond in the dimer, whilst the latter band has been attributed to a $d_\pi \longrightarrow \sigma^*$ transition.[2]

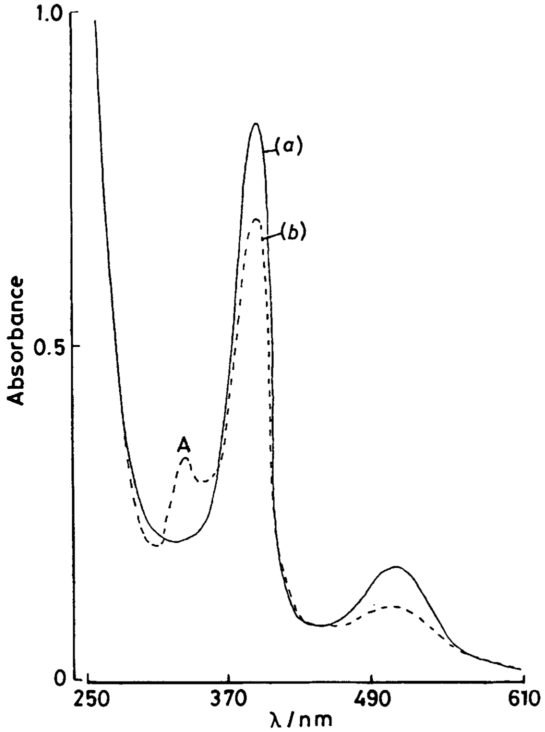


Figure 2. Ultraviolet–visible spectra from an experiment with $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in a pvc film (cast from a thf solution) at 12 K: (*a*) before irradiation; (*b*) after 15 min of irradiation ($\lambda > 400$ nm). Band marked A is for the photoproduct (see text)

Irradiation ($\lambda > 400$ nm) of the film with light corresponding to the visible absorption band produced four new bands (A) in the i.r. spectrum at 1 978, 1 933, 1 855, and 1 665 cm⁻¹ together with a band for free CO at 2 133 cm⁻¹, whilst the parent bands decreased in intensity [Figure 1(*b*)]. At the same time, a new band (A) grew in the electronic absorption spectrum [$\lambda_{max.}$ 330 nm; Figure 2(*b*)]. The parent i.r. band at 1 909 cm⁻¹ appeared to decrease at a slower rate than that at 1 955 cm⁻¹, suggesting that a further new band was growing under the former parent band. A fifth band (A) was subsequently revealed [ν_{CO} *ca.* 1 898 cm⁻¹, Figure 1(*c*)] on subtracting the remaining parent bands from the spectrum shown in Figure 1(*b*). After irradiation, the film was allowed to warm up in the dark. Warming to *ca.* 90 K led to reductions in all the new bands (A) and the band for free CO, whilst the bands for $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ increased in intensity. A complete reversal of the photoreaction occurred on warming the film to *ca.* 180 K [Figure 1(*d*)]. The relative intensities of the five new i.r. bands (A) remained constant throughout the experiment, indicating that they arose from a single photoproduct. The same product was observed on irradiation of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in pvc films at 12 K (or at 77 K) with light corresponding to the near-u.v. absorption band [$\lambda_{max.}$ 380 nm, Figure 2(*a*)]. It is evident from the observation of 'free CO' that the product is formed *via* dissociative loss of CO from the parent dimer. The i.r. spectrum

Table 1. Positions of i.r. (cm^{-1}) and near-u.v.–visible absorptions (nm) for some dinuclear group 6A metal carbonyl complexes and their photoproducts in pvc films at 12—298 K

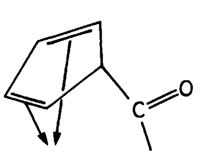
Complex	ν_{CO}/cm^{-1}	$\lambda_{max.}/nm$
$[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$	1 997, 1 944, 1 917, 1 900	475, 580
$[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_4]^a$	1 898, 1 874	395
$[Cr_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_3]^b$	1 812	345
$[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_3(thf)]^c$	1 920, 1 796, 1 762	360
$[Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$	1 871, 1 845	405
$[Cr_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_3]^b$	1 788	340
$[Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_3(thf)]^c$	1 881, 1 767, 1 728	350
$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$	2 010, 1 955, 1 909	380, 510
$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5]^b$	1 978, 1 933, 1 898, 1 855, 1 665	330
$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4]^a$	1 884, 1 854	320
$[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_6]$	1 985, 1 935, 1 898	395, 490
$[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_5]^b$	1 957, 1 908, 1 875, 1 833, 1 632	335
$[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]^a$	1 868, 1 838	320
$[Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl]^d$	2 052, 1 973	315
$[W_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$	2 002, 1 950, 1 900	360, 490
$[W_2(\eta^5\text{-}C_5H_5)_2(CO)_5]^b$	1 971, 1 925, 1 896, 1 838, 1 635	300
$[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4]^a$	1 880, 1 827	290
$[W(\eta^5\text{-}C_5H_5)(CO)_3Cl]^d$	2 045, 1 956	310

[a] Observed on irradiation of hexacarbonyl dimer at 298 K. [b] Observed at 12—77 K. [c] Observed on warming films from 12 K to *ca.* 100 K. [d] Data for authentic sample of this complex in a pvc film at 298 K.

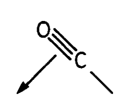
of this product [Figure 1(*c*)] shows five bands in the carbonyl stretching region. The band seen at 1 665 cm^{-1} occurs at a lower frequency than those normally observed for a terminal or bridging CO ligand. That this band arises from the vibration of a CO ligand in the photoproduct was confirmed, however, in separate experiments on irradiation of $[Mo_2(\eta^5\text{-}C_5H_5)_2(^{12}CO)_{6-n}(^{13}CO)_n]$ (n = 0—6) in pvc films at 12 K. Irradiation produced new bands in the i.r. spectrum at 1 665 and 1 625 cm^{-1}, corresponding to the vibrations of a ^{12}CO and ^{13}CO ligand, respectively.[*] The fact that five carbonyl i.r. absorptions (A) are observed [Figure 1(*c*)] suggests that the product is the dinuclear pentacarbonyl species $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$. The possibility that the product is $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5(thf)]$, arising from a reaction of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$ with residual thf solvent in the film, can be ruled out since the same product bands were also seen to form in films cast from 1,2-dichloroethane solutions.

Near-u.v. ($300 < \lambda < 400$ nm) or visible irradiation ($\lambda > 400$ nm) of the complexes $[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_6]$ and $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in pvc films at 12—77 K also led to the formation of CO-loss products. For example, irradiation into the near-u.v. absorption band ($\lambda_{max.}$ 395 nm) observed for the dimer $[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_6]$ (ν_{CO} 1 985w, 1 935s, and 1 898s cm^{-1}) produced free CO and the new species $[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_5]$ with five carbonyl i.r. absorptions at 1 957, 1 908, 1 875, 1 833, and 1 632 cm^{-1}. A new band ($\lambda_{max.}$ 335 nm) also appeared for the photoproduct in the electronic absorption spectrum. A complete reversal of the photoreaction was seen to occur on subsequently warming films to *ca.* 180 K. A pentacarbonyl species $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$, observed on irradiation of $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in films at 12—77 K, was similarly seen to recombine completely with CO on warming the films to *ca.* 180 K.

Spectroscopic data for the photoproducts $[M_2(\eta^5C_5H_5)_2(CO)_5]$ (M = Mo or W) and $[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_5]$, formed from the hexacarbonyl dimers in pvc films at 12—77 K, are listed in Table 1. The i.r. spectra of these products have some features resembling those of the parent dimers and the known tetracarbonyl dimers $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ (R = H or Me). For example, the intense band (A) observed for $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$ at 1 933 cm^{-1} [Figure 1(*c*)] is similar to the intense band seen at 1 955 cm^{-1} for the parent compound $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$, which only has terminal CO ligands.[15] Two of the other bands (A) at 1 898 and 1 855 cm^{-1} occur at similar wavenumbers to those observed for $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$,[†] which has semi-bridging CO ligands.[18] The low-frequency band (A) observed at 1 665 cm^{-1} for $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$ could be attributed to either an acyl group, formed by bonding of CO to a carbon atom of a C_5H_5 ring [shown in (*a*) below], or a bridging four-electron donor CO ligand which provides two σ electrons to one metal atom and two π electrons to the other [shown in (*b*)]. This type of bonding exists in the dimer $[(OC)_2Mn(Ph_2PCH_2PPh_2)_2(\mu\text{-}CO)Mn(CO)_2]$ (ν_{CO} 1 645 cm^{-1}).[19]



(*a*)



(*b*)

CO binding of type (*b*) seems more likely in view of the facile thermal reversal of the photoreactions at low temperatures (< 180 K) and the strong metal dependence of the i.r. band positions, *cf.* ν_{CO} 1 665 and 1 635 cm^{-1} for $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$ and $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$, respectively. The i.r. spectra suggest that the CO-loss products observed to form in the pvc films may have the structure (**2**) shown below, where dotted interaction represents a semibridging interaction.

In contrast with the photoreactions described above, near-u.v. ($300 < \lambda < 400$ nm) or visible irradiation ($\lambda > 400$ nm) of the complex $[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in pvc films at 12—77 K did not lead to the formation of a pentacarbonyl product.

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[*] The observed shift of 40 cm^{-1} to lower energy on substitution of a ^{12}CO ligand in the photoproduct by ^{13}CO is predicted from the Teller-Redlich rule.[17] Other bands attributable to the ^{13}CO-enriched product were observed in the region 1 950—1 800 cm^{-1} but were too broad to be resolved.

[†] This complex was seen to form on irradiation ($\lambda > 300$ nm) of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in films at 298 K (described later). Its i.r. spectrum in pvc films cooled to 77 K showed bands at 1 885 and 1 853 cm^{-1}.

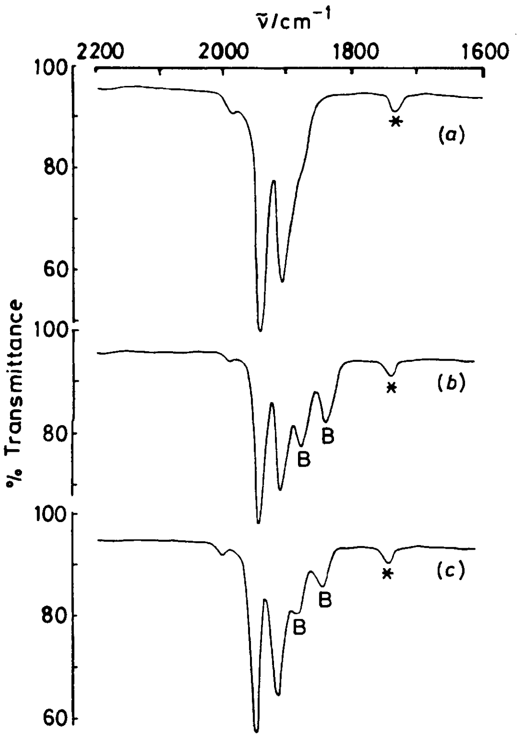
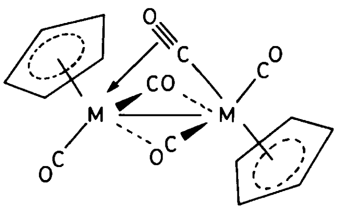


Figure 3. Infrared spectra from an experiment with $[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_6]$ in a pvc film (cast from a thf solution) at 298 K: (*a*) before irradiation; (*b*) after 10 min of irradiation (λ > 300 nm); (*c*) after leaving the film in the dark for 15 min. Bands marked B are for the photoproduct and that marked * is for ketone groups in pvc

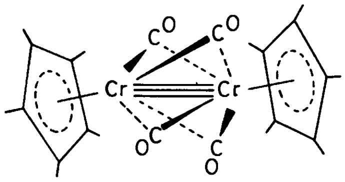


(2) M = Mo or W

Indeed, no photoreaction of the chromium dimer was observed at low temperatures.

Irradiation (λ > 300 nm) of $[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_6]$ in a pvc film at room temperature (298 K) produced a new species (B) with i.r. absorptions at 1 868 and 1 838 cm^{-1} [Figure 3(*a*) and (*b*)] and a near-u.v. absorption at *ca.* 320 nm. A thermal reversal of the photoreaction occurred on subsequently leaving the film in the dark [Figure 3(*c*)]. The photoproduct (B) is identified from its i.r. spectrum as the complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$, observed ($\nu_{CO}$ 1 874 and 1 846 cm^{-1}) on irradiation (λ > 300 nm) of $[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_6]$ in argon-purged pentane solutions.[1] The reversal of the photoreaction in the film evidently arises from recombination of CO with the photoproduct. Although CO could not be detected in films irradiated at room temperature, it was observed (ν_{CO} 2 133 cm^{-1}) on cooling the films to 77 K.* Irradiation of the dimers $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ (M = Cr, Mo, or W) in pvc films at room temperature similarly led to the formation of the tetracarbonyl dimers $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (Tables 1 and 2). The complexes $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ and $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ were seen to react with CO in the films after irradiation, regenerating the parent dimers. However, the chromium tetracarbonyl dimer was not observed to back react with CO and persisted in the films at room temperature. Other photoproducts, besides the tetracarbonyl dimers, were detected after irradiation (λ > 300 nm) of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ and $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in pvc films at room temperature. These products (M = Mo, ν_{CO} 2 052 and 1 973 cm^{-1}; M = W, ν_{CO} 2 045 and 1 956 cm^{-1}) were identified as the complexes $[Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ and $[W(\eta^5\text{-}C_5H_5)_2(CO)_3Cl]$ from spectroscopic data obtained for authentic samples of these compounds in pvc films (Table 1).

(*ii*) *Photolysis of* $[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ *and* $[Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$.—Figure 4(*a*) shows the i.r. spectrum of the tetracarbonyl dimer $[Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$ at 12 K in a pvc film (4 mg per 500 mg) cast from a thf solution (298 K). Two bands are seen at 1 871 and 1 845 cm^{-1}. These bands can be assigned to antisymmetric carbonyl stretching vibrations (A_u modes) of the dimer which has the centrosymmetric structure (3) (C_i symmetry) containing semibridging CO ligands.[20] The electronic absorption spectrum of the dimer in the film showed a band in the visible region ($\lambda_{max.}$405 nm).



(3)

Irradiation of the film with visible light (λ > 350 nm) produced a new band in the electronic absorption spectrum at *ca.* 340 nm. At the same time a new band (C) appeared in the i.r. spectrum at 1 788 cm^{-1}, along with a band for free CO, whilst the parent bands decreased in intensity [Figure (4(*b*)]. No new bands were observed in the region 2 000—1 800 cm^{-1}, even after subtracting the parent bands from the spectrum. On subsequently warming the film from *ca.* 70 to 100 K the bands for the parent complex increased in intensity whilst those for the product (C) and for free CO decreased. The parent band at 1 871 cm^{-1} appeared to increase more rapidly than that at 1 845 cm^{-1} and new bands (D) grew in the spectrum at 1 767 and 1 728 cm^{-1} [Figure 4(*c*)]. The change observed in the relative intensities of the parent bands on warming the film could be attributed to the growth of another new band (D) at *ca.* 1 881 cm^{-1}, which was revealed on subtracting the parent bands from the spectrum [Figure 4(*d*)]. On further warming the film to *ca.* 120 K the photoproduct band (C) at 1 788 cm^{-1} disappeared whilst the new bands (D) increased in intensity. The latter bands subsequently disappeared on warming the film to *ca.* 200 K which led to complete regeneration of the parent complex $[Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$ [Figure 4(*e*)]. The relative intensities of the new i.r. bands (D) remained constant throughout the experiment, indicating that they arose from a single species.

The photoreaction observed at 12 K was also seen to occur on irradiation of $[Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$ in pvc films cast from 1,2-dichloroethane solutions. The observation that free CO is produced during irradiation indicates that the photoproduct (C) is a CO-loss product. The fact that the i.r. spectrum of this product shows only one carbonyl stretching band (ν_{CO} 1 788 cm^{-1}) and that this band occurs in the bridging-carbonyl

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* Carbon monoxide molecules rotate freely in polymer films at room temperature which gives rise to a rotation–vibration i.r. spectrum whose intensity cannot be observed if only a small amount of CO is present. At 77 K, however, the molecules do not rotate and a sharp '*Q*' branch line is observed.

Table 2. Positions of i.r. (cm^{-1}) and near-u.v.–visible absorptions (nm) for some dinuclear Group 8 metal carbonyl complexes and their photoproducts in pvc films at 12— 298 K

Complex	ν_{CO}/cm^{-1}	$\lambda_{max.}$/nm
cis-$[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (bridged)	1 995, 1 955, 1 808, 1 775	275, 460
(non-bridged)	2 010, 1 931	330, 460
trans-$[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (bridged)	1 955, 1 775	275, 460
(non-bridged)	1 965, 1 931	330, 460
$[Ru(\eta^5\text{-}C_5H_5)(CO)_2Cl]^{a,b}$	2 052, 1 998	290
trans-$[Ru_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]^c$	1 922, 1 750	280, 462
$[Ru(\eta^5\text{-}C_5Me_5)(CO)_2Cl]^{a,b}$	2 030, 1 985	285
$[Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CO)_2]$	1 877, 1 829	370, 500
$[Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CO)]^d$	1 804	—

[a] Data for authentic sample of this complex in a pvc film at 298 K. [b] Observed at 298 K. [c] Complex only exists in *trans* CO-bridged form. [d] Observed at 12 K.

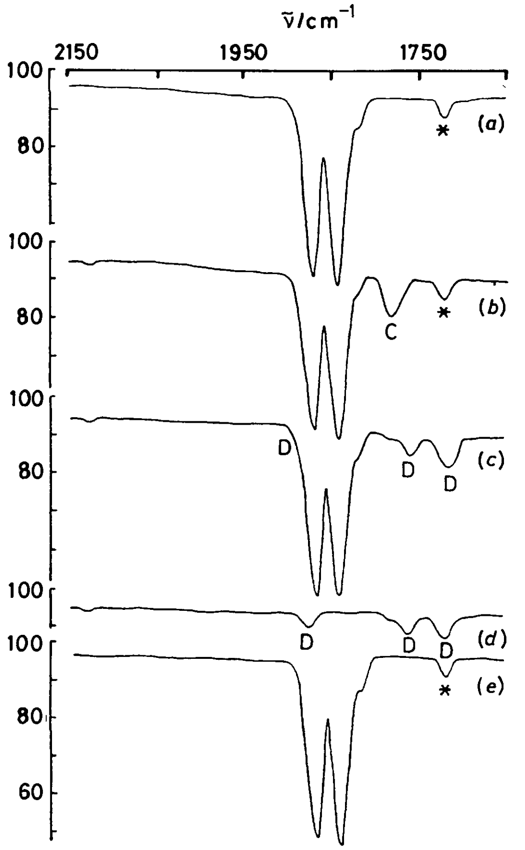
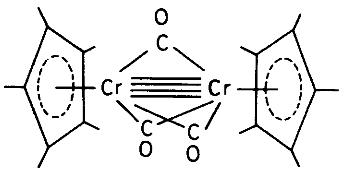


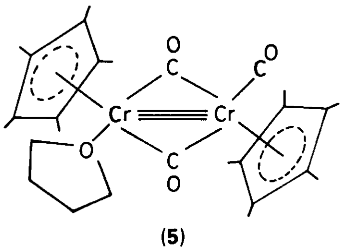
Figure 4. Infrared spectra from an experiment with $[Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$ in a pvc film (cast from a thf solution) at 12 K: (*a*) before irradiation; (*b*) after 20 min of irradiation (λ > 350 nm); (*c*) after warming the film to *ca.* 100 K; (*d*) spectral subtraction (*c*) – *N*(*a*), where *N* is a scaling factor; (*e*) after warming the film to *ca.* 200 K. Bands marked C and D are for products and that marked * is for ketone groups in pvc

stretching region suggests that the product may be the symmetric species (**4**) (D_{3h} symmetry) with three equivalent bridging CO ligands (see below). The i.r. spectrum of this species is expected to show a single band in the carbonyl stretching region corresponding to a degenerate (*E*′) carbonyl vibration. The eighteen-electron rule[21,22] would require this species to have a Cr$\equiv$Cr quadruple bond. It was not possible to confirm the symmetric structure of the photoproduct (**4**) using ^{13}CO labelling of the parent dimer owing to the broad overlapping i.r. bands observed for the product in pvc films. Photolysis of $[Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_{4-n}]$ (n = 0—4) in frozen gas matrices, where sharper i.r. absorptions are expected, could not be carried out since the dimer decomposed on subliming.



(**4**)

The new product (D), generated on warming the pvc film cast from a thf solution [Figure 4(*c*)], was not seen to form in films cast from 1,2-dichloroethane solutions. This product evidently arises from a reaction of the photogenerated species (C) with thf. The fact that three carbonyl i.r. bands (D) are observed suggests that the product is the complex $[Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_3(thf)]$, with three CO ligands. Two of the bands (D) at 1 767 and 1 728 cm^{-1} occur in the bridging-carbonyl region at lower wavenumbers than the bands seen for the photoproduct (C) [structure (**4**)] and the parent compound $[Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$, which has semibridging CO ligands [structure (**3**)]. The other band (ν_{CO} 1 881 cm^{-1}) is at a higher wavenumber than for the parent dimer bands and could arise from either a terminal or semibridging CO ligand. A possible structure (**5**) for the product (D), based on its i.r. spectrum, is shown below.



(**5**)

By analogy with the reactions described above, near-u.v.–visible irradiation (λ > 320 nm) of the complex $[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (Tables 1 and 2) in pvc films at 12 K produced free CO and a new species having one bridging-CO i.r. absorption (ν_{CO} 1 812 cm^{-1}). This product is proposed to be the triply CO-bridged dimer $[Cr_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_3]$ [*cf.* structure (**4**)]. On warming the films to *ca.* 80 K this species was seen to recombine with CO or react with thf in the films, regenerating the parent dimer or forming the complex $[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_3(thf)]$, respectively (Table 1).

No photoproducts were detected on irradiation (λ > 300 nm) of $[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ or $[Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$ in pvc films at room temperature (298 K).

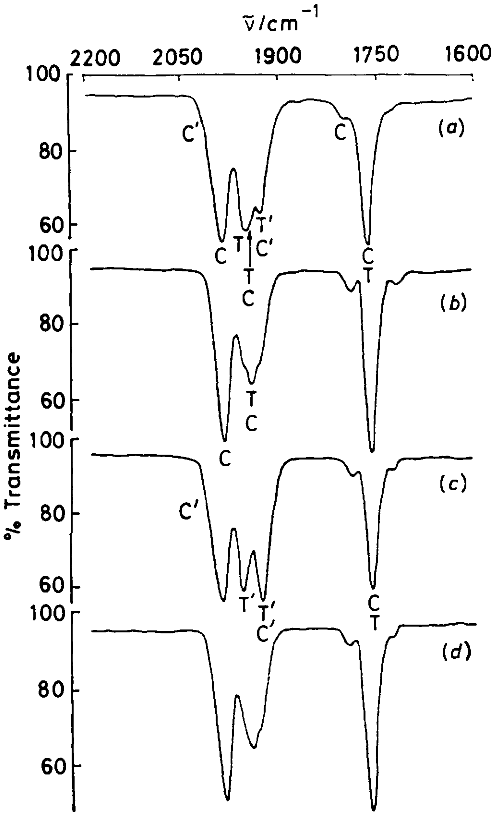
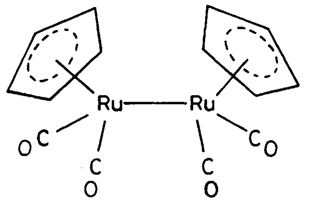


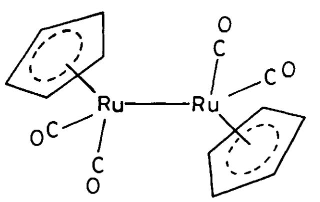
Figure 5. Infrared spectra from an experiment with $[Ru_2(\eta^5-C_5H_5)_2(CO)_4]$ in a pvc film (cast from a thf solution): (*a*) at 298 K; (*b*) after cooling the film to 12 K; (*c*) after 15 min of irradiation ($\lambda > 300$ nm) of the film at 12 K; (*d*) after warming the film to *ca.* 40 K. Bands C and T are for *cis* and *trans* bridged isomers of $[Ru_2(\eta^5-C_5H_5)_2(CO)_4]$, C′ and T′ for non-bridged isomers

(*iii*) *Photolysis of* $[Ru_2(\eta^5-C_5R_5)_2(CO)_4]$ (R = H *or* Me).—Figure 5(*a*) shows the i.r. spectrum of the complex $[Ru_2(\eta^5-C_5H_5)_2(CO)_4]$ at room temperature (298 K) in a pvc film (3 mg per 500 mg) cast from a thf solution (298 K). The spectrum is similar to that observed[23] for the dimer in polar solvents, *e.g.* CH_2Cl_2. The dimer exists as *cis* and *trans* non-bridged isomers[23] [structures (**6**) and (**7**)] in equilibrium with CO-bridged isomers [structures (**8**) and (**9**)], analogous to those observed for $[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$ in solution [24] and in pvc films.[10] The bands C and T seen in the i.r. spectrum at 1 995, 1 955 (sh), 1 808, and 1 775 cm^{-1} can be assigned to the *cis* and *trans* bridged isomers, whilst the bands C′ and T′ seen at 2 010 (sh), 1 965, and 1 931 cm^{-1} are assigned to the *cis* and *trans* non-bridged isomers, respectively, by analogy with the solution spectra obtained previously.[23]

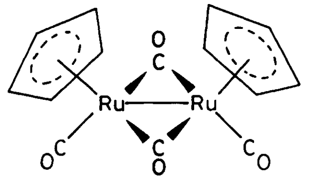
The electronic absorption spectrum of $[Ru_2(\eta^5-C_5H_5)_2(CO)_4]$ in a pvc film at room temperature [Figure 6(*a*)] shows two bands in the near-u.v. region with maxima at 275 and 330 nm. These bands are assigned to $\sigma \longrightarrow \sigma^*$ (Ru–Ru) transitions in the CO-bridged and non-bridged isomers, respectively, again by analogy with reported solution spectra.[7] Cooling the film to 12 K [Figures 5(*b*) and 6(*b*)] resulted in some conversion of the non-bridged isomers of the dimer into the bridged isomers. Subsequent irradiation ($\lambda > 300$ nm) of the film at 12 K led to an increase in the bands for the *cis* and *trans* non-bridged isomers, whilst the bands for the bridged isomers decreased in intensity [Figures 5(*c*) and 6(*c*)], *i.e.* the bridged isomers undergo photoinduced 'bridged opening.' A complete reversal of the photoreaction was observed on warming the film to *ca.* 40 K [Figure 5(*d*)]. No i.r. spectroscopic evidence for a CO-loss product, *e.g.* $[Ru_2(\eta^5-C_5H_5)_2(\mu-CO)_3]$, was obtained on near-u.v. ($290 < \lambda < 400$ nm) or visible irradiation ($\lambda > 400$ nm) of $[Ru_2(\eta^5-C_5H_5)_2(CO)_4]$ in pvc films at 12—77 K, in contrast with the photoreaction of $[Fe_2(\eta^5-C_5H_5)_2(CO)_4]$ observed previously in similar pvc films.[10] No photoreactions were observed at all on irradiation ($\lambda > 290$ nm) of the complex *trans*-$[Ru_2(\eta^5-C_5Me_5)_2(CO)_4]$ in films at 12—77 K.



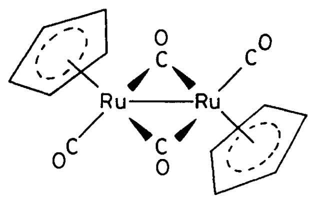
(**6**) *cis* (C_{2v} symmetry)



(**7**) *trans* (C_{2h} symmetry)



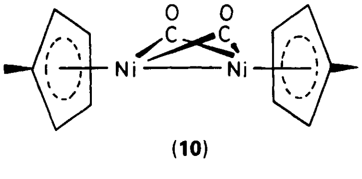
(**8**) *cis* (C_{2v} symmetry)



(**9**) *trans* (C_{2h} symmetry)

Near u.v–visible irradiation of the dimers $[Ru_2(\eta^5-C_5R_5)_2(CO)_4]$ (R = H or Me) in pvc films at room temperature led to the formation of the mononuclear complexes $[Ru(\eta^5-C_5R_5)(CO)_2Cl]$. These products were identified on the basis of their i.r. spectra obtained for authentic samples of the complexes in pvc films or in solutions.[7,25]

(*iv*) *Photolysis of* $[Ni_2(\eta^5-C_5H_4Me)_2(\mu-CO)_2]$.—Figure 7(*a*) shows the i.r. spectrum of the complex $[Ni_2(\eta^5-C_5H_4Me)_2(\mu-CO)_2]$ at 77 K in a pvc film (3 mg per 500 mg) cast under N_2 from a thf solution (298 K). The spectrum is very similar to that recorded for the dimer[26] in CH_2Cl_2 solution. By analogy with the solution spectra,[26] the bands seen in the spectrum at 1 877 and 1 829 cm^{-1} can be assigned respectively, to symmetric and antisymmetric carbonyl stretching vibrations of the dimer which has the CO-bridged structure (**10**) (C_i symmetry) shown below.[25] The electronic absorption spectrum of this complex in the film at 77 K showed bands with maxima at *ca.* 370 and 500 nm.



(**10**)

Irradiation of the film with light corresponding to the band at 500 nm produced free CO and a new species (E) showing one bridging CO i.r. absorption band at 1 804 cm^{-1} [Figure 7(*b*)]. This species was only formed in a low yield and no new bands were detected in the electronic absorption spectrum. The same product (E) was seen to form on irradiating (at 77 K) the near-u.v. absorption band ($\lambda_{max.}$ 370 nm) observed for the parent dimer. On subsequently warming the film to *ca.* 150 K [Figure 7(*c*)] the product band (E) and the band for free CO disappeared whilst the parent bands increased in intensity, indicating that the photoreaction was thermally reversible. The photoproduct (E) is evidently formed by dissociative loss of CO from the parent dimer $[Ni_2(\eta^5-C_5H_4Me)_2(\mu-CO)_2]$. The fact

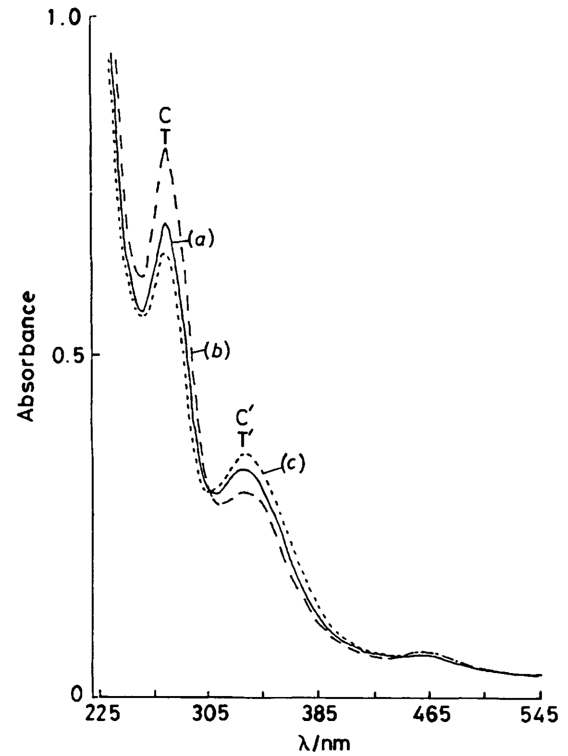


Figure 6. Ultraviolet–visible spectra from an experiment with $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in a pvc film (cast from a thf solution): (*a*) at 298 K; (*b*) after cooling the film to 12 K; (*c*) after 15 min of irradiation ($\lambda > 300$ nm) of the film at 12 K. Bands C and T are for *cis* and *trans* isomers of $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$, C′ and T′ for non-bridged isomers

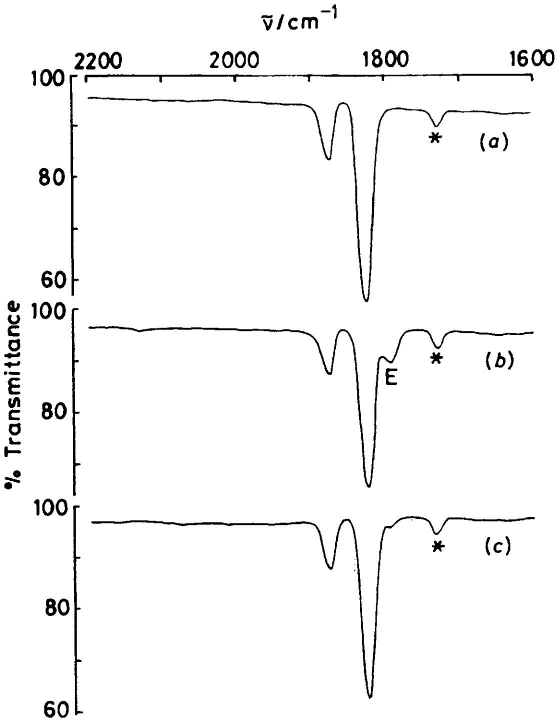
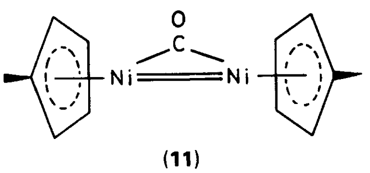


Figure 7. Infrared spectra from an experiment with $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(CO)_2]$ in a pvc film (cast from a thf solution) at 77 K: (*a*) before irradiation; (*b*) after 20 min of irradiation ($\lambda > 400$ nm); (*c*) after warming the film to *ca.* 150 K. Band E is for the photoproduct and that marked * is for ketone groups in pvc



(11)

that this product has only one bridging CO stretching band in the i.r. spectrum suggests that it has the structure (**11**) shown below. This CO-loss product is depicted as having a Ni=Ni double bond, in accordance with the eighteen-electron rule.[21,22] The possibility that the product (E) is $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(CO)(thf)]$, generated in a reaction of $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(CO)]$ with thf in the film, can be ruled out since the same product was seen to form on irradiation ($\lambda > 400$ nm) of $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CO)_2]$ at 77 K in a pvc film cast from a 1,2-dichloroethane solution.

Discussion

The dimers $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CO)_2]$, $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_6]$ (M = Mo or W, R = H or Me) and $[Cr_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ (R = H or Me) undergo loss of a CO ligand on irradiation ($\lambda > 300$ nm) in pvc films at 12—77 K.

The dinuclear species formed in these reactions recombine with CO in films at temperatures in the range 70—200 K and are evidently very unstable. The proposed structures of the chromium, molybdenum, and tungsten species are very similar to those of some known stable compounds. The species $[Mo_2(\eta^5\text{-}C_5R_5)_2(CO)_5]$ and $[W_2(\eta^5\text{-}C_5R_5)_2(CO)_5]$ [structure (**2**)] have a structure analogous to that of the dimer $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}CN)]^-$, which has semi-bridging CO ligands and a cyano-bridging ligand donating two σ electrons to one metal atom and two π electrons to the other.[27] The CO-loss products $[Cr_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}CO)_3]$ [structure (**4**)], produced on photolysis of the $[Cr_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ complexes (R = H or Me), can be compared with the known compound $[Cr_2(\eta^5\text{-}C_6H_6)_2(\mu\text{-}CO)_3]$ (ν_{CO} 1 770 cm^{-1}; $\lambda_{max.}$ 300 nm) which has a symmetric structure (D_{3h} symmetry) and which has been formulated as having a Cr≡Cr triple bond.[28] The triply CO bridging structure is interestingly analogous to that of $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_3]$ formed in pvc films, glasses, and even Nujol mulls[29] at 12—77 K.

The observation that the dimer $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in pvc films at 12—77 K undergoes loss of CO on irradiation with either near-u.v. or visible light is consistent with the results obtained in the early flash photolysis study[9b] where evidence for a CO-dissociation pathway was obtained [*cf.* equation (4)]. The stoicheiometry proposed[9] for the CO-loss product is the same at that of the photoproducts formed in the pvc films at 12—77 K. In fact the electronic absorption spectrum of the species $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$ formed on photolysis of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in films shows a band in the near-u.v. region ($\lambda_{max.}$ 330 nm). The CO-loss product detected on flash photolysis of the hexacarbonyl dimer also absorbs in the region 300—350 nm.[9b] This suggests that the product observed in the films is the same as that detected in the flash photolysis study.

Irradiation ($\lambda > 300$ nm) of the dimers $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_6]$ and $[Ru_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ (M = Mo or W, R = H or Me) in pvc films at 298 K leads to the formation of the complexes $[M(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ and $[Ru(\eta^5\text{-}C_5R_5)(CO)_2Cl]$, respectively. These products are the same as those observed on irradiation ($\lambda > 300$ nm) of the parent dimers in chlorocarbon solvents.[6,7,25] The reactions in solution have been proposed[6,7] to involve radical species, *e.g.* $[Mo(\eta^5\text{-}C_5H_5)\text{-}$

$(CO)_3]^\bullet$, produced *via* photoinduced cleavage of the metal–metal bond in the parent dimers [*cf.* equation (1)] and which abstract chlorine atoms from the solvent molecules. Although a flash photolysis study[9b] of the photochemistry of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in solution has provided evidence for the formation of the species $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]^\bullet$, no i.r. spectroscopic evidence for radicals* was obtained on irradiation ($\lambda > 300$ nm) of the molybdenum, tungsten, or ruthenium dimers in pvc films at 12—77 K. The photoconversion of these dimers into the chloro compounds observed in films at room temperature could, however, proceed *via* a radical pathway. It is possible that the dimers do undergo metal–metal bond cleavage when irradiated in the films at 12—77 K but that the resulting radicals are unable to separate in the rigid polymeric medium and recombine immediately to regenerate the parent compounds. No photoreaction is seen to occur on irradiation ($\lambda > 300$ nm) of the dimer $[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in pvc films at 12—77 K. However, photoinduced cleavage of the Cr–Cr bond in this complex may occur, with the $[Cr(\eta^5\text{-}C_5H_5)(CO)_3]^\bullet$ radicals rapidly recombining within the polymeric 'cage.'

Interestingly, the CO-bridged dimers $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ and $[Ru_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$, unlike $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$, do not undergo loss of CO on irradiation ($\lambda > 300$ nm) in pvc films at 12—77 K. The *cis* and *trans* bridged isomers of $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ do, however, photochemically rearrange in films at 12 K to form the non-bridged isomers. Photoinduced 'CO bridge opening' in the dimers $[Ru_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ (R = H or Me), and similarly for $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$, could be the primary process involved in the conversion of these compounds into the chloro complexes in pvc films irradiated at room temperature. No evidence for 'CO bridge opening' was obtained on irradiation ($\lambda > 300$ nm) of *trans*-$[Ru_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$ in films at 12 K. However, non-bridged isomers of this dimer, which have not been observed in solution or in the solid state, are thought to be sterically disfavoured.[22,31] Thermal or photochemical cleavage of the metal–metal bond in such isomers could occur in solution or in the pvc films at room temperature leading to the formation of radicals. In the films at 12 K, however, metal–metal bond cleavage may be inhibited by the rigid medium and thus any photogenerated non-bridged isomers may immediately rearrange to the more stable parent (bridged) isomers. The *cis* and *trans* non-bridged isomers of $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in fact *thermally* rearrange to the bridged isomers in films at temperatures as low as 40 K.

Irradiation ($\lambda > 300$ nm) of the complexes $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ (M = Cr, Mo, or W) in pvc films at room temperature results in the formation of the M≡M triple bonded dimers $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ as well as the chloro compounds $[M(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ (M = Mo or W). The dinuclear products are the same as those formed on irradiation of the parent dimers in hydrocarbon solvents.[1] It is reasonable to suggest that the $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ complexes (M = Mo or W) could arise from photoinduced loss of CO from $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$, observed on irradiation ($\lambda > 300$ nm) of the hexacarbonyl dimers in films at 12—77 K. The tetracarbonyl dimers were not, however, seen to form from $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$ in these films. The photoconversion of $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ into $[M_2(\eta^5\text{-}C_5H_5)(CO)_4]$ (M = Cr, Mo, or W) in solution has been proposed to involve thermal CO loss from photogenerated $[M(\eta^5\text{-}C_5H_5)(CO)_3]^\bullet$ radicals followed by coupling of two $[M(\eta^5\text{-}C_5H_5)(CO)_2]^\bullet$ radicals, *i.e.* equations (5)—(7).[1]

$$[M_2(\eta^5\text{-}C_5H_5)_2(CO)_6] \xrightarrow{h\nu} 2[M(\eta^5\text{-}C_5H_5)(CO)_3]^\bullet \quad (5)$$

$$[M(\eta^5\text{-}C_5H_5)(CO)_3]^\bullet \longrightarrow [M(\eta^5\text{-}C_5H_5)(CO)_2]^\bullet + CO \quad (6)$$

$$2[(\eta^5\text{-}C_5H_5)M(CO)_2]^\bullet \longrightarrow [(OC)_2(\eta^5\text{-}C_5H_5)M{\equiv}M(\eta^5\text{-}C^5H^5)(CO)_2] \quad (7)$$

The fact that the tetracarbonyl dimers are seen to form in pvc films irradiated at 298 K but not at 12—77 K is consistent with this mechanism. It is interesting, however, that the complexes $[Mo_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ (R = H or Me) and $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ thermally back react with CO films at room temperature [equation (8)]. Indeed the photoconversion of

$$[M_2(\eta^5\text{-}C_5R_5)_2(CO)_4] \xrightarrow[2CO]{\text{Heat}} [M_2(\eta^5\text{-}C_5R_5)_2(CO)_6] \quad (8)$$

$[M_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ into $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (M = Mo or W) has only been observed previously[1] in solutions purged with argon or nitrogen. The possibility that the thermal reactions [equation (8)] proceed *via* a radical pathway [*cf.* a reversal of the reaction steps (5)—(7)] seems unlikely since this would have to involve cleavage of the M≡M triple bond in the $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ complexes.† Regeneration of the hexacarbonyl dimers [equation (11)] could, alternatively, involve stepwise addition of CO to the M≡M triple bond in the tetracarbonyl dimers, *via* $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_5]$ [*cf.* structure (**2**)].

The fact that irradiation ($\lambda > 300$ nm) of the dimers $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CO)_2]$, $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ (M = Mo or W), and $[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in pvc films at 12—77 K leads to loss of a CO ligand is interesting in view of the photosubstitution reactions of these complexes in solution. Visible irradiation ($\lambda > 400$ nm) of $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CO)_2]$ in the presence of acetylene in solution is known[33] to lead to the formation of the alkyne-bridged complex $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}HC{\equiv}CH)]$. This reaction could involve initial co-ordination of acetylene to the species $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CO)]$ [structure (**11**)]. Furthermore the triply CO bridged species $[Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_3]$ [structure (**4**)] may be an intermediate in the photoreaction of $[Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$ with ^{13}CO [equation (9)] observed in pentane solutions.[33] Indeed, the species

$$[Cr_2(\eta^5\text{-}C_5Me_5)_2(^{12}CO)_4] \xrightarrow[^{13}CO]{h\nu} [Cr_2(\eta^5\text{-}C_5Me_5)_2(^{12}CO)_3(^{13}CO)] + CO \quad (9)$$

$[Cr_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}CO)_3]$ (R = H or Me) react with CO or with thf in pvc films at temperatures above *ca.* 70 K. The $[Cr_2(\eta^5\text{-}C_5R_5)_2(CO)_3(thf)]$ complexes [structure (**5**)] proposed to form in the films might be generated *via* thermal CO bridge opening in the species $[Cr_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}CO)_3]$ (**4**) followed by bonding of thf to the co-ordinatively unsaturated metal centre.

The CO photosubstitution reactions of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ observed in hydrocarbon solvents[3] have been proposed[5] to involve substitution of CO in $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]^\bullet$ radicals photogenerated from the parent dimer. This mechanism was based on the observation that both mono- and di-

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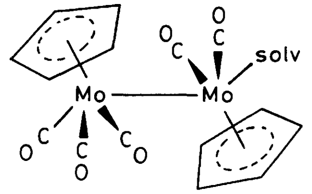
* Infrared spectra have been reported[30] for the species $[M(\eta^5\text{-}C_5H_5)(CO)_3]^\bullet$ (M = Mo, ν_{CO} = 2 009 and 1 912 cm^{-1}; M = W, ν_{CO} = 1 999 and 1 898 cm^{-1}) generated on photolysis of the hydrido complexes $[M(\eta^5\text{-}C_5H_5)(CO)_3H]$ in CO matrices at 12 K. The spectrum of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^\bullet$ produced on flash photolysis of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in a cyclohexane solution showed bands at 2 004 and 1 938 cm^{-1}.[12]

† Such a process is not expected to be sufficiently facile at room temperature to account for the observed reactivity of the complexes $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ (M = Mo or W) towards CO. Kinetic studies[32] have shown that even the singly M–M bonded dimer $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ does not undergo facile thermal M–M bond cleavage in solution at room temperature.

substituted products, *e.g.* $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(PPh_3)_2]$ and $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5(PPh_3)]$, are formed in the solutions.[3] The monosubstituted complexes, could, in fact, arise from a direct reaction of the phosphine ligands with the photogenerated CO-loss product, *i.e.* $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$. The CO-loss product (**2**) generated in the pvc films at 12—77 K did not react with thf on warming the films to 200 K. However, in solutions at room temperature, these products could adopt different structures having a vacant co-ordination site available for donor ligands to bond to the metal centre. In potentially co-ordinating solvents, *e.g.* MeCN, the CO-loss intermediates may exist as $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5(solv)]$ (solv = solvent), *cf.* structure (**12**) below. The fact that a pentacarbonyl species is not formed on irradiation ($\lambda > 300$ nm) of $[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in pvc films at 12—77 K suggests that the latter complex does not undergo photoinduced loss of CO, at least under the above irradiation conditions. Indeed photosubstitution of CO in $[Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ by donor ligands in solution has not been observed,[34] in contrast with the photoreactions of the molybdenum and tungsten dimers.



(**12**)

Conclusions

The dinuclear complexes $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CO)_2]$, $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_6]$ (M = Mo or W, R = H or Me), and $[Cr_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ undergo dissociative loss of a CO ligand on irradiation ($\lambda > 300$ nm) in pvc films at 12—77 K. The i.r. spectra of the CO-loss products $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_5]$, formed on irradiation of the $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_6]$ complexes in the films, suggest that these products have two terminal and two semibridging CO ligands and a bridging four-electron donor CO ligand. Irradiation of the tetracarbonyl dimer $[Cr_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ (R = H or Me) in the films at 12—77 K leads to the formation of the triply CO bridged complex $[Cr_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}CO)_3]$. The singly CO bridged compound $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CO)]$ is formed on irradiation of the dimer $[Ni_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}CO)_2]$.

The near-u.v.–visible absorption of the species $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$ ($\lambda_{max.}$ 330 nm) in the pvc films occurs at the same wavelength as that of the CO-loss product detected previously on flash photolysis of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ in hydrocarbon solvents. This suggests that the product detected in the flash photolysis studies was also the CO-bridged dimer.

The *cis* and *trans* CO-bridged isomers of the complex $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ photochemically rearrange to the non-bridged isomers on irradiation ($\lambda > 300$ nm) in pvc films at 12 K. Similar irradiation of the complexes $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ (M = Mo or W) and $[M'_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ (M′ = Fe or Ru; R = H or Me) in films at 298 K results in the formation of the mononuclear compounds $[M(\eta^5\text{-}C_5H_5)(CO)_3Cl]$ and $[M'(\eta^5\text{-}C_5R_5)(CO)_2Cl]$, by analogy with the photoreactions observed in chlorocarbon solvents. These reactions may involve photoinduced cleavage of the M–M bond in the parent dimers. In the reactions of the CO-bridged parent compounds $[Fe_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$ and $[Ru_2(\eta^5\text{-}C_5R_5)_2(CO)_4]$, photoinduced 'CO bridge opening' {observed on irradiation of $[Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in films at 12 K} may also be involved.

The CO photosubstitution products observed on irradiation of the complexes $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_6]$ (M = Mo or W) in presence of donor ligands L (*e.g.* PPh_3) in solution could arise from reactions of the ligands L with the species $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_5]$, rather than from substitution of CO in photogenerated $[M(\eta^5\text{-}C_5H_5)(CO)_3]^{\bullet}$ radicals, as previously proposed.[7]

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