Photochemistry of some Binuclear Carbonyl Compounds of Manganese, Rhenium, Molybdenum, and Tungsten, and of some Related Pentacarbonylmetal Halides in *n*-Donor Solvents

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On irradiation in solvents of high donicity, the binuclear carbonyl compounds $[M_2(CO)_{10}]$ (M = Mn or Re) and $[\{M(\eta\text{-}C_5H_5)(CO)_3\}_2]$ (M = Mo or W) undergo efficient photoheterolysis leading to a metal carbonyl anion; related carbonylmetal halides $[M(CO)_5X]$ (M = Mn or Re, X = Cl, Br, or I) on similar treatment also give rise to the corresponding carbonyl anion.

MECHANISTIC investigation of metal carbonyl photochemistry has concentrated on CO-loss reactions of simple metal carbonyls, carbonyl anions, and also arene-metal carbonyls, and there has been less emphasis on structurally more complex systems.[1] However, recent developments have included examination of binuclear carbonyls in solution such as the photolyses (*i*) of $[Mn_2(CO)_{10}]$ in tetrahydrofuran (thf) and CCl_4 solutions to give respectively $[Mn(CO)_5]^{\cdot}$ [2] and $[Mn(CO)_5Cl]$,[3] (*ii*) of tungsten and molybdenum carbonyl amines (to give luminescence [1]), and (*iii*) of cyclopentadienyliron carbonyl halides, to give products of the type $[Fe(\eta\text{-}C_5H_5)L]X$ [4,5] or $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ [6] (L = entering ligand, X = halogen).

While typical behaviour of the binuclear carbonyl species in solvents of low dielectric constant such as chloroform or thf is to undergo homolysis, *viz.* [equation (1) [where R = η-C_5H_5, $P(OEt)_3$, or CO] as evinced by

$$[\mathrm{R(OC)}_n\mathrm{M{-}M(CO)}_n\mathrm{R}] \xrightarrow{h\nu} 2[\dot{\mathrm{M}}(\mathrm{CO})_n\mathrm{R}] \qquad (1)$$

spin-trapping of the $[\dot{M}(CO)_nR]$ species,[7,8] we have noted some tendency for both thermolysis and photolysis of such compounds to proceed *via* heterolysis either in donor solvents or in the presence of donor ligands, *e.g.* the formation of $[Mn(py)_6][Mn(CO)_5]_2$ from $[Mn_2(CO)_{10}]$ on heating in pyridine solvent [9] and the production of $[Mo(\eta\text{-}C_5H_5)(CO)_2(PPh_3)][Mo(\eta\text{-}C_5H_5)(CO)_3]$ on irradiating $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$ in benzene in the presence of an excess of PPh_3.[10] Here we report the results of irradiating binuclear carbonyls of Mn, Re, Mo, and W in solvents of high *n*-donicity, confirming a general tendency towards photoheterolysis under such conditions. We have also examined the photochemistry in these solvents of some further carbonylmetal halides related to the binuclear compounds.

RESULTS AND DISCUSSION

Following our earlier work [6,11] on the photochemistry of metal carbonyl derivatives, we have examined the behaviour of binuclear compounds, beginning with pyridine solutions of $[Mn_2(CO)_{10}]$. This carbonyl, on irradiation in CCl_4 solution,[3] undergoes a homolytic metal–metal bond cleavage to give $[Mn(CO)_5]^{\cdot}$. On the other hand, the thermal reaction of the same compound in pyridine solvent yields $[Mn(py)_6][Mn(CO)_5]_2$ by a heterolytic disproportionation.[9]

Irradiation at $\lambda = 400 \pm 70$ nm of $[Mn_2(CO)_{10}]$ in

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[1] M. S. Wrighton, *Chem. Rev.*, 1974, **74**, 401.

[2] S. A. Hallock and A. Wojcicki, *J. Organometallic Chem.*, 1973, **54**, C27.

[3] M. S. Wrighton and D. S. Ginley, *J. Amer. Chem. Soc.*, 1975, **97**, 2065.

[4] R. B. King, W. C. Zipperer, and M. Ishaq, *Inorg. Chem.*, 1972, **11**, 1361.

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[6] L. H. Ali, A. Cox, and T. J. Kemp, *J.C.S. Dalton*, 1973, 1475.

[7] A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, *J.C.S. Chem. Comm.*, 1974, 966.

[8] P. J. Krusic, H. Stoklosa, L. E. Manzer, and P. Meakin, *J. Amer. Chem. Soc.*, 1975, **97**, 667.

[9] W. Hieber and W. Schropp, jun., *Z. Naturforsch.*, 1960, **B15**, 271.

[10] R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1968, 43.

[11] D. M. Allen, A. Cox, T. J. Kemp, and L. H. Ali, *J.C.S. Dalton*, 1973, 1899.

pyridine solution (0.01 mol dm^{-3}) induced fundamental structural changes as shown in the i.r. spectral profile summarised in Table 1 (the new strong bands appearing at 1 893 and 1 857 cm^{-1} are particularly notable). In order to determine whether the essential requirement for such a transformation is that the solvent should have a high co-ordinating power, as measured by the donicity parameter,[12] similar experiments were carried out in further media. The results obtained are summarised in Table 1 from which it can be seen that in dimethyl sulphoxide (dmso) of donicity 29.8 [12] and *NN*-dimethylformamide (dmf) of donicity 26.6 [12] the salient features of the (product) i.r. spectra are closely similar in both cases to that derived from pyridine (donicity 33.1),[12] although there are differences in detail, *e.g.* the minor bands (1 964 and 1 923 cm^{-1}) in dmf solution, which were barely produced during bare-arc irradiation (Figure 1). In contrast, in dioxan and cumene, solvents of much lower donicity, a quite different product appears to be formed, and in dioxan reaction was very slow. The principal i.r. bands obtained with high-donicity solvents compare exactly with those for an authentic sample [9] of $[Mn(py)_6][Mn(CO)_5]_2$, strongly suggesting that the $[Mn(CO)_5]^-$ anion is responsible for the emergent i.r. bands during photolysis. A typical i.r. spectral profile is illustrated in Figure 1. A minor feature apparent in most runs, being conspicuous only in cumene solvent, is the appearance of a sharp band at *ca.* 2 340 cm^{-1} due presumably to CO_2. The chemical origin of this side-product is unclear.

TABLE 1

Irradiation of $[Mn_2(CO)_{10}]$ in solvents of different donicity

Solvent	$\tilde{\nu}_{max.}$/cm^{-1} before photolysis	$\tilde{\nu}_{max.}$/cm^{-1} after photolysis	Irradiation time (t/s)
Pyridine	2 040vw, 2 050vs, 2 012vs, 2 000vs, 1 973w	2 040m, 1 893vs, 1 857vs	275
dmso	2 048vs, 2 009vs, 2 000vs, 1 970 (sh)	2 340vw, 1 895vs, 1 860vs	300
dmso (saturated with CO gas)	2 048vs, 2 009vs, 2 000vs, 1 970 (sh)	2 340w, 1 895vs, 1 860vs	
dmf	2 345vw, 2 051vs, 2 012vs, 2 000vs, 1 974w	2 345m, 1 964m 1 923w, 1 895vs, 1 862vs	400
Dioxan	2 050vs, 2 012vs, 2 000vs, 1 970m	2 343m, 2 050vs, 2 012vs, 2 000vs, 1 970m, 1 680s	540
Cumene	2 050vs, 2 013vs, 2 000vs, 1 977s	2 340vs, 1 688m	190

Supporting evidence for a heterolytic path comes from e.s.r. studies. The e.s.r. spectra of solutions of $[Mn_2(CO)_{10}]$ in dmso and dmf after irradiation at 77 K for up to 2 h displayed a broad weak singlet: however, after warming the matrix to room temperature, a six-line spectrum emerged with $a_{av.}$ = 9.48 mT. Recooling the solution to 77 K had no effect on the signal. In an analogous experiment using pyridine as solvent, no signal could be detected at 77 K or after warming to room temperature, but photolysis of a sample at 293 K produced a six-line spectrum ($a_{av.}$ 8.94 mT). These coupling patterns and hyperfine coupling constants are typical of those of Mn^{2+} in water, and the spectrum of an authentic sample of $[Mn(dmso)_6][ClO_4]_2$ in dmso solution was identical to that of the photolysate of $[Mn_2(CO)_{10}]$ in the same solvent. These observations contrast with those of Hallock and Wojcicki who report [2] that photolysis (λ 350 nm) of $[Mn_2(CO)_{10}]$ in thf produces a paramagnetic species ($a_{av.}$ 9.3 mT) which is claimed to be $[Mn(CO)_5]^{\bullet}$. In view of our findings, it seems probable that this assignment is unfounded, a conclusion also drawn by Wrighton and Ginley [3] on other grounds.

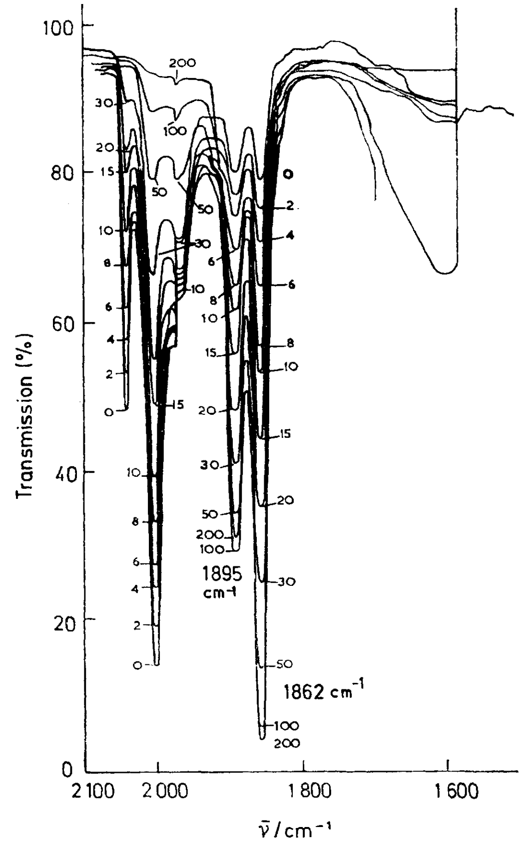

FIGURE 1 I.r. spectral profile for the 400 ± 70-nm irradiation of $[Mn_2(CO)_{10}]$ in dmf solution. Numbers refer to irradiation times (t/s)

That the primary photochemical process of binuclear metal carbonyls is expected on theoretical grounds to be homolytic metal–metal bond cleavage has been discussed elsewhere,[3] and this expectation is borne out by experiments employing weakly polar solvents. However, in view of the fact that a net heterolysis occurs in the solvents we have employed, it is clear that medium effects are highly influential. Although the product pattern fails to distinguish between a primary act of photoheterolysis [equation (2)] or a radical disproportionation follow-

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[12] V. Gutmann, *Chem. in Britain*, 1971, 7, 102.

ing a primary photohomolysis [equation (3)], the higher

$$[Mn_2(CO)_{10}] \xrightarrow{h\nu} [Mn(CO)_5]^+(solv) + [Mn(CO)_5]^-(solv) \quad (2)$$

$$2[Mn(CO)_5]^{\cdot} \longrightarrow [Mn(CO)_5]^+(solv) + [Mn(CO)_5]^-(solv) \quad (3)$$

quantum yields for destruction of decacarbonyl in py, dmso, and dmf compared with cumene or dioxan, apparent from the i.r. spectral profiles, supports (2) in preference to (3).

The results of an analogous series of investigations on rhenium decacarbonyl, $[Re_2(CO)_{10}]$, are compiled in Table 2. The general resemblance between the i.r. spectra of the photolysate of both $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$ in the solvents mentioned implies an analogous photoheterolysis to give a salt of the $[Re(CO)_5]^-$ anion, which has [13] $\nu_{max.}$ at 1 910 and 1 864 cm^{-1}.

In order to demonstrate the possible generality of photoheterolysis as a primary photochemical process for metal–metal bond cleavage in media of high donicity, we examined both $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$ and $[\{W(\eta\text{-}C_5H_5)(CO)_3\}_2]$. The photoexcited molybdenum dimer has recently been shown [14] to react efficiently with halide (X^-) ion in acetone solution to give a net disproportionation to $[Mo(\eta\text{-}C_5H_5)(CO)_3X]$ and $[Mo(\eta\text{-}C_5H_5)(CO)_3]^-$. Our results (Table 3) indicate that both dimers are exceedingly photolabile at room temperature and undergo very similar transformations in all the solvents listed. The i.r. spectral profiles for both reactions were very complex, but one feature common to all experiments is the production of intense bands at *ca.* 1 895 and 1 770 cm^{-1} (Figure 2) attributable to $[M(\eta\text{-}C_5H_5)(CO)_3]^-$ ($\nu_{max.}$ at 1 895 and 1 770 cm^{-1} in solution),[14] indicating a net photoheterolysis. This assignment was confirmed by preparation [15] of $[NEt_4][Mo(\eta\text{-}C_5H_5)(CO)_3]$, the i.r. spectrum of which in pyridine shows a pattern below 2 000 cm^{-1}, with particularly strong bands at 1 893 and 1 773 cm^{-1}, identical to those present after irradiation of $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$ in pyridine. Moreover, the ^1H n.m.r. spectrum of the authentic anion in $[^2H_5]$pyridine exhibited a sharp singlet at τ 5.0, whilst the photolysate showed a singlet at τ 5.1. {Burkett *et al.*[14] give τ 5.0 for $[Mo(\eta\text{-}C_5H_5)(CO)_3]^-$ in acetone solution.} The tungsten dimer $[\{W(\eta\text{-}C_5H_5)(CO)_3\}_2]$, which, as already stated, shows an i.r. spectral profile on photolysis closely similar to that of the molybdenum complex, is believed to undergo photoheterolysis to give the corresponding anion $[W(\eta\text{-}C_5H_5)(CO)_3]^-$.

TABLE 2

Irradiation of $[Re_2(CO)_{10}]$ in solvents of different donicity

Solvent	$\tilde{\nu}_{max.}/cm^{-1}$ before photolysis	after photolysis	Irradiation time (t/s)
Pyridine	2 072s, 2 010vs, 1 963m	1 994w, 1 880m	3 600
dmf	2 075s, 2 010vs, 1 964m	1 908s, 1 884m	500

An investigation was also made of the photochemistry of the related simple mononuclear carbonylmetal halides, $[M(CO)_5X]$ (M = Mn or Re; X = Cl, Br, or I) excluding $[Re(CO)_5I]$. The results of these photolyses are shown in Table 4, from which it can be seen that the photolysates displayed intense i.r. bands at *ca.* 1 895 and 1 860 cm^{-1}, typical of the $[M(CO)_5]^-$ anion. In the case of $[MnBr(CO)_5]$ a larger-scale anaerobic photolysis led to an isolable crystalline product identified by comparison with authentic material [9] as $[Mn(py)_6][Mn(CO)_5]_2$. This behaviour is in contrast to the reported photochemistry of $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$ (X = Cl or Br) in which photoelimination of halide occurs to give the dimer $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$, and also to the photochemistry of $[M(\eta\text{-}C_5H_5)(CO)_3Cl]$ (M = Mo or W) from which the binuclear complex $[\{Mo(\eta\text{-}C_5H_5)(CO)_2Cl\}_2]$ is formed and which leads on further irradiation to i.r. spectral changes consistent with the replacement of a CO ligand by solvent.[6]

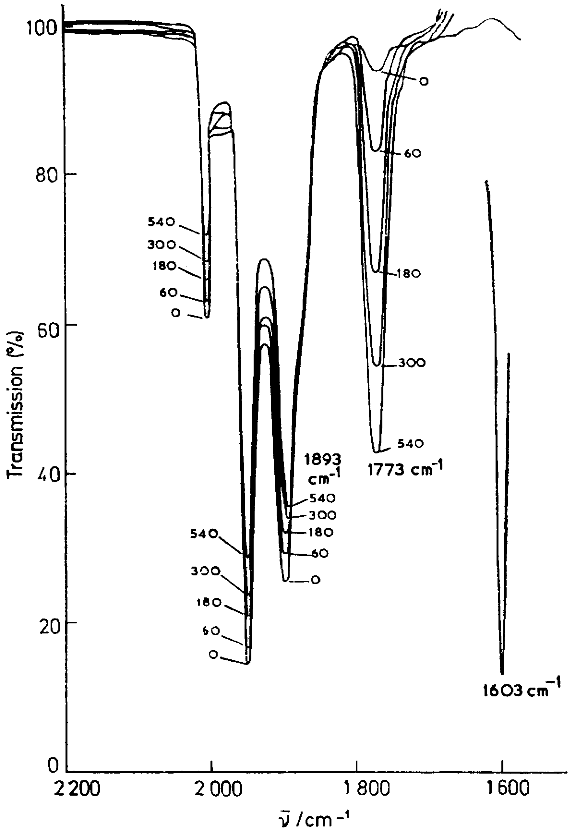

FIGURE 2 I.r. spectral profile for the 400 ± 70-nm irradiation of $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$ in pyridine solution. Numbers refer to irradiation times (t/s)

Quantum yields of substrate disappearance were

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[13] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 1962, **1**, 933.

[14] A. R. Burkett, T. J. Meyer, and D. G. Whitten, *J. Organometallic Chem.*, 1974, **67**, 67.

[15] R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometallic Chem.*, 1966, **5**, 341.

measured for four dimeric compounds under anaerobic conditions (Table 5) In the cases of the compounds of Mo and W the product had a small but significant absorption at the wavelength used for the determination (493 nm). To circumvent this problem, a special computer program was written in co-operation with Dr. P. Moore, the details of which are to be published elsewhere.[16] All the quantum yields are in the 0.1—1.0 region, showing that these photoreactions are highly efficient processes. An investigation of the reaction media in darkness revealed that background ' thermal ' reactions, while detectable at room temperature, were insignificant on the time scale of the photolyses, *e.g.* [{Mo(η-C_5H_5)$(CO)_3$}$_2$] decomposed to an extent of 5% in 16 h in dmso solution. The decomposition rate was faster in pyridine solution (especially when solutions were exposed to the heating effect of the analysing beam of the i.r. spectrophotometer) and was of the same order as the photodecomposition rate in $P(NMe_2)_3O$ solution (which was therefore abandoned as a working solvent). An accelerating effect of dissolved O_2 was noted in the case of the molybdenum dimer in dmso solution (when the final optical density was zero, indicating fast decomposition of the product absorbing at 493 nm found in the anaerobic runs).

TABLE 3

Irradiation of [{Mo(η-C_5H_5)$(CO)_3$}$_2$] and [{W(η-C_5H_5)$(CO)_3$}$_2$] in solvents of differing donicity

Compound	Solvent	$\tilde{\nu}_{max}$/cm^{-1} before photolysis	$\tilde{\nu}_{max}$/cm^{-1} after photolysis	Irradiation time (t/min)
[{Mo(η-C_5H_5)$(CO)_3$}$_2$]	dmso	2 002s, 1 998m, 1 948vs, 1 902vs	2 050s, 1 948m, 1 895vs, 1 825w, 1 772vs, 1 650br, s	2
	dmf	2 006s, 1 998w, 1 948vs, 1 906vs	2 049s, 1 955s, br 1 895vs, 1 825m, 1 770vs	5
	Pyridine	2 335vw, 2 006s, 1 953vs, 1 901vs	2 335s, 1 953m, 1 893vs, 1 773vs	42
[{W(η-C_5H_5)$(CO)_3$}$_2$]	dmso	2 000s, 1 946vs, 1 895vs	2 040s, 1 919s, 1 890vs, 1 800w, 1 768vs	15
	dmf	2 002vs, 1 944vs, 1 895vs	2 040s, 2 015m, 1 920s, 1 893vs, 1 805w, 1 770vs	30
	Pyridine	2 335 vw, 2 005s, 1 948vs, 1 895vs	2 335m, 2 015s, 1 908s, 1 890s, 1 830 (sh), 1 770vs, 1 675s	55

TABLE 4

Irradiation of [$M(CO)_5X$] (M = Mn or Re, X = Cl, Br, or I) but excluding [$Re(CO)_5I$], in solvents of different donicity

Compound	Solvent	$\tilde{\nu}_{max.}$/cm^{-1} before photolysis	$\tilde{\nu}_{max.}$/cm^{-1} after photolysis	Time (t/s)
[$Mn(CO)_5Cl$]	dmso	2 335w, 2 140vw, 2 085 (sh), 2 043vs, 2 000s, 1 995w, 1 975 (sh), 1 925m, 1 900m, 1 855 (sh)	2 335m, 2 025 (sh), 2 010w, 1 975m, 1 975 (sh), 1 925 (sh), 1 895s—m, 1 860s	8
	dmf	2 335m, 2 139vw, 2 087 (sh), 2 042vs, 2 005vs, 1 995m, 1 983 (sh), 1 922m	2 335m, 2 010s, 1 970m, 1 925s, 1 900vs, 1 860s	29
	Pyridine	2 335w, 2 140w, 2 087 (sh), 2 048vs, 2 025w, 1 995m, 1 993m, 1 900m	2 335s, 2 025s, 1 935s, 1 900s	5
[$MnBr(CO)_5$]	dmso	2 335m, 2 135w, 2 083w, 2 040s, 2 023 (sh), 2 005vs, 1 995 (sh), 1 973s, 1 925vs, 1 900s	2 335m, 2 023s, 2 005 (sh), 1 970w, 1 925w, 1 900s, 1 860 (sh)	30
	dmf	2 340s, 2 140w, 2 089m, 2 045vs, 2 012vs, 1 970vs, 1 920vs	2 340s, 2 012w, 1 970w, 1 950w, 1 920w, 1 890s, 1 855vs	2 400
	Cumene	2 140m, 2 055vs, 2 005s, 1 998s	2 340s, 2 140vw, 2 055w, 2 005w, 1 998w	1 080
[$Mn(CO)_5I$]	dmf	2 340vw, 2 135s, 2 050vs, 2 010vs, 2 001vs, 1 970 (sh)	2 340s, 2 085w, 2 050w, 2 010s, 2 001s, 1 970vs, 1 923vs, 1 895vs, 1 860vs	500
[$Re(CO)_5Cl$]	dmso	2 085 (sh), 2 035vs, 1 975m	2 002m, 1 992m, 1 956vw, 1 900vw, 1 870vs, 1 702s, 1 655m, br	6 000
	dmf	2 087 (sh), 2 035vs, 1 977m	2 035vw, 1 996s, 1 959m, 1 903s, 1 879m	2 500
	Pyridine	2 085 (sh), 2 038vs, 1 975s	2 035vw, 2 021s, 1 975w, 1 906m, 1 880s	2 760
[$ReBr(CO)_5$]	dmso	2 150w, 2 070 (sh), 2 035vs, 2 005 (sh), 1 975m, 1 875 (sh)	2 150m, br, 2 035w, 2 005m, 1 975 (sh), 1 885s, 1 865s, 1 636vs, br	3 900
	dmf	2 150w, 2 086 (sh), 2 035vs, 1 983m, 1 900 (sh)	2 035 (sh), 1 995m, 1 955w, 1 887vs, 1 863s	3 600
	Pyridine	2 150w, 2 086 (sh), 2 038vs, 1 978m, 1 910 (sh), 1 860 (sh)	2 335m, 2 038 (sh), 2 023vs, 1 978 (sh), 1 910 (sh), 1 880vs	3 500

These results, taken together with those of our earlier papers, indicate that in a considerable number of cases the photochemistry of organometallic compounds is critically affected by change of solvent, new paths ap-

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[16] T. J. Kemp and P. Moore, unpublished work.

pearing in the group of solvents typified by pyridine, dmso, dmf, and also $P(NMe_2)_3O$.

TABLE 5

Quantum yields for the photodecomposition of binuclear carbonyl compounds

Compound	λ(irradiation)/nm	Solvent	ϕ(decomposition)
$[Mn_2(CO)_{10}]$	**364**	Pyridine	**0.19**
		dmso	**0.15**
		dmf	**0.14**
$[Re_2(CO)_{10}]$	**311**	dmso	**0.65**
$[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$	**493**	Pyridine	**0.79**
		dmso	**0.27**
		dmso [a]	**0.56**
		dmso [b]	**0.58**
		dmf	**0.53**
$[\{W(\eta\text{-}C_5H_5)(CO)_3\}_2]$	**493**	Pyridine	**1.00**
		dmso	**0.32**
		dmf	**0.53**

[a] Aerated solution. [b] Oxygenated solution.

EXPERIMENTAL

Phototransformations were monitored principally by i.r. spectroscopy, using a Perkin-Elmer model 621 instrument. Samples (*ca.* 10^{-2} mol dm^{-3}) were contained in i.r. cells fitted with a Teflon spacer (thickness, 0.1 mm) and NaCl windows. These samples were irradiated ***in situ*** and the spectra were recorded at measured time intervals. Irradiation was provided by a 200-W point-source high-pressure mercury arc as supplied by Wotan, the output of which was passed through a blue-glass filter transmitting a band centred at 400 nm (total bandwidth, 140 nm) or through a Balzer metal interference filter. Quantum yields were measured by previous procedures:[17] the light from the 200-W lamp was filtered through a suitable Balzer filter, isolating the 364 ± 10-nm line for $[Mn_2(CO)_{10}]$, the 311 ± 10-nm line for $[Re_2(CO)_{10}]$, and the 493 ± 10-nm line for the compounds of Mo and W described below. The optical decay of the material under investigation was measured using a Cary 14 spectrophotometer over at least two half-lives, and the data were processed by means of a curve-fitting program developed here.[16]

N.m.r. spectra were recorded after photolysing the $[^2H_6]$-dimethyl sulphoxide solutions in an n.m.r. tube, and were obtained using a Perkin-Elmer R 12(B) spectrometer. All solutions were deoxygenated before photolysis by flushing with nitrogen.

The compounds $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$ were supplied by Strem Chemicals and used without further purification. The following compounds were prepared by literature methods: $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$;[18] $[\{W(\eta\text{-}C_5H_5)(CO)_3\}_2]$; $[Mn(CO)_5Cl]$;[19] $[MnBr(CO)_5]$;[20] $[Mn(CO)_5I]$;[21] $[Re(CO)_5Cl]$;[22] and $[ReBr(CO)_5]$.[13] The first two compounds were purified by column chromatography followed by crystallisation from chloroform, and, with the exception of $[Mn(CO)_5I]$ which was crystallised directly using chloroform, the remaining compounds were purified by sublimation at 0.1 mmHg and 20 °C.*

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

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