Photochemistry of Acetylacetonato-, Trifluoroacetylacetonato-, and Hexafluoroacetylacetonato-dicarbonyl-rhodium and -iridium Complexes in Frozen Gas Matrices at 12 K. Infrared Spectroscopic Evidence for Carbon Monoxide Dissociation and Chelate Ring-opening Processes †

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Infrared spectroscopic evidence, including ^{13}CO labelling and energy-factored CO force-field fitting, is presented to show that on photolysis of $[M(CO)_2L]$ (L = RCOCHCOR′; R,R′ = CH_3 or CF_3; M = Rh or Ir) complexes at high dilution in CH_4, Ar, CO, and N_2 matrices at 12 K new species [M(CO)L], $[M(CO)_2(L^*)]$ (L* = unidentate form of L), and $[M(CO)(N_2)L]$ are produced. The results are discussed in relation to the mechanisms of thermal reactions in solution. In particular, the reversibility of the reaction $[M(CO)_2L] \rightleftharpoons [M(CO)L] + CO$ and the dominance of this reaction indicates that the hitherto discounted dissociative pathway should be reconsidered. Some evidence is also found for the chelate ring opening to give $[M(CO)_2(L^*)]$ species, but no evidence was found for expanded-co-ordination-number species corresponding to the previously proposed associative mechanism for ligand-exchange and substitution reactions.

Substitution of carbonyl groups in complexes of the type $[Rh(CO)_2L]$ (L = β-diketonate) by olefins *or* partially by PPh_3 and $AsPh_3$ has resulted in [Rh(CO)(L)L′].[1] Ligand-exchange studies on four-co-ordinate complexes of the type $[M(L)L'_2]$ show that they may react differently compared to the complexes of the type $[M(\eta^5-C_5H_5)L'_2]$. For example, the complexes $[M(acac)(C_2H_4)_2]$ (M = Rh or Ir, acac = acetylacetonate) [2-4] have been shown to react in solution by a S_N2 associative mechanism, while for $[M(\eta^5-C_5H_5)L'_2]$ (M = Rh, L′ = C_2H_4 or CO;[2,3,5] M = Co, L′ = CO or PPh_3) [6,7] a dissociative S_N1 mechanism has been suggested for their solution reactions. It has been reported, however, that CO exchange with $[Co(\eta^5-C_5H_5)(CO)_2]$ is extremely rapid at 25 °C involving a bimolecular S_N2 associative mechanism.[8] In this case changes in the co-ordination of the cyclopentadienyl ring may play a direct part in the CO exchange mechanism.[9] In gas matrices no evidence has been found for the formation of $[Co(\eta^5-C_5H_5)(CO)]$ and CO on photolysis of $[Co(\eta^5-C_5H_5)(CO)_2]$ and the existence of an equilibrium involving an associative reaction forming $[Co(\eta^3-C_5H_5)(CO)_3]$ in a CO matrix has been demonstrated.[10]

The existence of a short-lived radical species as the intermediate in both isomerisation and decomposition reactions of *trans*-$[Rh(tfa)_3]$ (tfa = 1,1,1-trifluoroacetylacetonate) has been shown by flash-photolysis studies.[11,12] Although these studies could not provide any structural information, it has been suggested that the intermediate species corresponds to a short-lived radical where one of the ligands has become a unidentate. Intermediates that involve bond breaking between the metal and the β-diketone have been suggested in the isomerisation and substitution reactions of metal–β-diketone complexes.[13-15] The synthesis of a semi-chelating metal–β-diketone complex [16] containing one short and one long metal–oxygen bond may provide a model for transition states in these complexes.

Matrix-isolation studies have been shown to be very useful for investigating photochemical reactions and for characterising reactive species.[17] In this paper, we report the results of i.r. studies on the photochemistry of the complexes $[M(CO)_2L]$ [L = acac, tfa, or 1,1,1,5,5,5-hexafluoroacetylacetonate (hfa); M = Rh or Ir] in inert (Ar, CH_4) and reactive (CO, N_2) gas matrices at 12 K, using the terminal CO-stretching region to identify species.‡ Some preliminary results on the $[Rh(tfa)(CO)_2]$ complex have been reported earlier.[18]

Experimental

Cryogenic temperatures (*ca.* 12 K) were obtained using a Displex CSA-202 closed-cycle helium refrigeration system (Air Products & Chemicals Inc.). Matrices of $[M(CO)_2L]$ complexes were prepared by a slow-deposition technique employing the apparatus described elsewhere.[19] Vapour from the solid held at a known temperature was co-condensed with matrix gas onto a cooled CaF_2 window. Spray-on temperatures of the solid varied between −5 °C for $[Rh(hfa)(CO)_2]$ and 40 °C for $[Ir(acac)(CO)_2]$ in accordance with the volatilities observed in vapour-pressure measurements.[20] Monomer isolation (*ca.* 1 : 2 000) was ensured by having a substantially higher gas flow for the host matrix gas than for the complex to be isolated. Deposition was monitored throughout by running i.r. spectra of the matrix using a Grubb-Parsons Spectromajor grating spectrometer modified to have a grating change at 1 850 cm^{-1} rather than at 2 000 cm^{-1} (Southampton) and a Beckman 4250 grating spectrometer (Amsterdam). Calibration in the region 1 530—2 200 cm^{-1} was carried out regularly using the gas-phase absorption of CO, DCl, and H_2O. Resolution was better than 1 cm^{-1} and the reproducibility of measurements was ±0.5 cm^{-1}. U.v. spectra were recorded on a Cary 14 spectrophotometer (Amsterdam) and a Pye-Unicam 1800 B spectrometer (Southampton).

The photolysis sources used were a Coherent ion laser

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† *Non-S.I. units employed:* Torr = (101 325/760) Pa; atm = 101 325 Pa.

‡ Bands attributable to the β-diketone ligands were considerably weaker than those of the carbonyl ligands. Because of the modest conversion into photoproducts, therefore, it proved impossible to monitor their formation with the conventional spectrometers at our disposal (see Discussion).

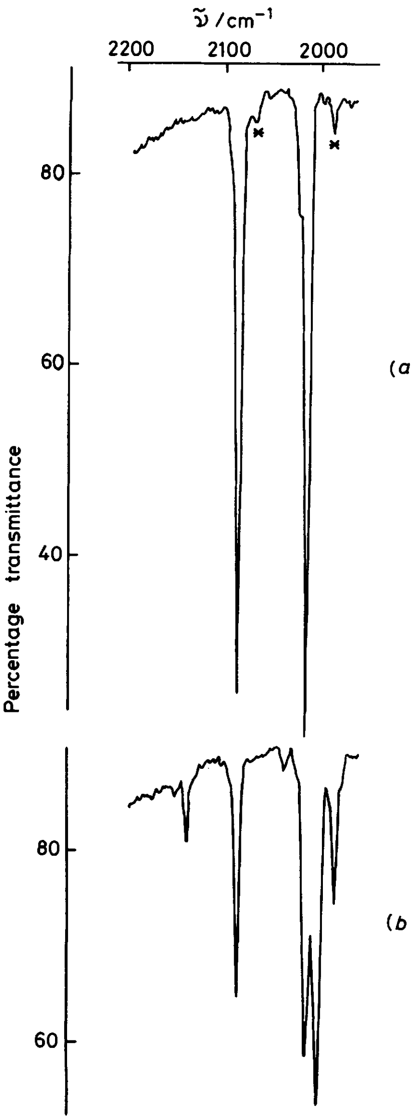


Figure 1. Infrared spectra from an experiment with $[Rh(acac)(CO)_2]$ isolated at high dilution in a CH_4 matrix at 12 K: (*a*) after deposition; (*b*) after photolysis for 5 h using the laser. Bands marked * are due to $[Rh(acac)(^{12}CO)(^{13}CO)]$ in natural abundance

(model 53, wavelength 351 nm) (Amsterdam) and a water-cooled medium-pressure mercury lamp (Philips HPK, 125 W) (Southampton). Wavelength-selective photolysis with the mercury lamp was achieved using the following combinations of absorbing materials: filter A, $280 < \lambda < 370$ nm and $\lambda > 550$ nm, quartz gas cell (pathlength 25 mm) containing Br_2 gas (300 Torr) + Pyrex glass disc (thickness 2 mm); filter B, $\lambda > 410$ nm, Corning filter 3391; filter C, $\lambda < 280$ nm and $\lambda > 550$ nm, quartz gas cell (pathlength 25 mm) containing Br_2 gas (300 Torr) + quartz gas cell (pathlength 25 mm) containing Cl_2 gas (2 atm).

Matrix gases (Ar, CH_4, CO, and N_2) were of grade ' X ' purity (BOC Ltd.) and ^{13}C-enriched CO (95%) was obtained from BOC Prochem Ltd.

The complexes $[M(CO)_2L]$ were prepared according to the literature methods [2,4,21,22] and purified by recrystallisation and sublimation. Their purities were checked by elemental analysis.

Table 1. Infrared band positions (cm⁻¹) for $[M(CO)_2L]$ complexes and their photoproducts in gas matrices at 12 K in the terminal CO-stretching region

Complex	CH_4	Ar	CO	N_2
$[Rh(acac)(CO)_2]$	2 086.0	2 087.4	2 089.5	2 090.0
	2 023.1 2 015.8 } [a]	2 016.1	2 021.9	2 022.1
$[Rh(tfa)(CO)_2]$	2 094.8	2 094.8	2 097.2	2 100.0
	2 028.9	2 028.0	2 031.9	2 034.0
$[Rh(hfa)(CO)_2]$	2 102.6	2 108.4		2 109.0
	2 039.5	2 046.2		2 046.6
$[Ir(acac)(CO)_2]$	2 075.1			
	2 001.6			
$[Ir(tfa)(CO)_2]$	2 085.4			
	2 011.0			
$[Rh(acac)(CO)]$	2 002.9	1 994.6	[b]	
$[Rh(tfa)(CO)]$	2 013.7	2 016.0 2 013.0 } [a]	2 012.0 [c]	2 019.6
$[Rh(hfa)(CO)]$	2 029.9	2 035.0		
$[Ir(acac)(CO)]$	2 026.0			
$[Ir(tfa)(CO)]$	2 033.1			
$[Rh(acac)(CO)(N_2)]$				2 242.2 (ν_{NN})
				2 028.3 (ν_{CO})
$[Rh(tfa)(CO)(N_2)]$				2 248.0 (ν_{NN})
				2 041.7 (ν_{CO})
$[Rh(hfa)(CO)(N_2)]$				2 260.0 (ν_{NN})
				2 052.2 (ν_{CO})
$[Rh(acac^*)(CO)_2]$ [d]	2 041.9	2 048.1		2 046.6
	1 988.0	1 989.4	[b]	1 985.3
$[Rh(tfa^*)(CO)_2]$ [d]	2 055.8	2 054.7	[b]	2 058.2
	1 966.7	1 998.0		1 998.3
$[Rh(hfa^*)(CO)_2]$ [d]	2 076.9	2 080.3		2 091.2
	2 011.2	2 011.0		2 011.0

[a] Matrix splitting. [b] Not detected. [c] Long photolysis time (15 h) required. [d] Asterisk indicates unidentate ligand.

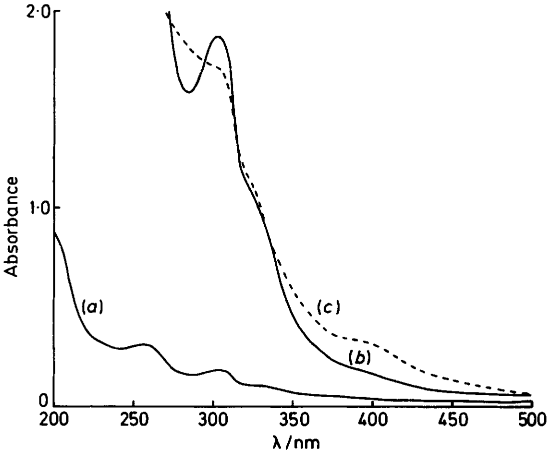


Figure 2. Ultraviolet-visible spectra from an experiment with $[Rh(acac)(CO)_2]$ isolated at high dilution in a CH_4 matrix at 12 K: (*a*) after deposition (15 min); (*b*) after further deposition for 60 min; (*c*) after photolysis for 2 h using the mercury arc and filter A

Results

Photolysis of $[Rh(CO)_2L]$ *Complexes in* Ar *and* CH_4 *Matrices.*—The i.r. spectra of $[Rh(CO)_2L]$ complexes isolated at high dilution in Ar and CH_4 matrices show two terminal CO-stretching bands [Figure 1(*a*), Table 1] corresponding to the symmetric A_1 (or A') and antisymmetric B_1 (or A'') modes expected for molecules with C_{2v} (or C_s) local symmetry together with two weaker bands (marked with an asterisk)

Table 2. Ultraviolet–visible absorption band positions (nm)[a] for $[M(CO)_2L]$ complexes after deposition and irradiation in matrices at 12 K, together with data for the complexes in solution[b] at 293 K

Complex	Matrix	After deposition	After irradiation[c]
$[Rh(acac)(CO)_2]$	CH_4	256s, 300m, 305 (sh)	395vw
	Ar	255s, 295m, 304 (sh)	400vw
	CO	257s, 299m, 306 (sh)	400vw
	N_2	256s, 297m, 304 (sh)	395vw
	Solution	258s, 301m, 323 (sh)	
$[Rh(tfa)(CO)_2]$	CH_4	240s, 252 (sh), 311m	400vw
	Ar	240s, 253 (sh), 310m	400vw
	CO	242s, 256 (sh), 315m	400vw
	N_2	247s, 251 (sh), 312m	400vw
$[Rh(hfa)(CO)_2]$	CH_4	245s, 313m	445vw
	Ar	246s, 315m	450vw
	N_2	247s, 316m	450vw
$[Ir(acac)(CO)_2]$	CH_4	251s, 290m, 330w 371w, 410w	
	Solution	261s, 297m, 339w 375 (sh), 412vw	
$[Ir(tfa)(CO)_2]$	CH_4	252s, 292m, 330w 370w, 410w	

[a] Relative intensities: v = very, w = weak, m = medium, s = strong, sh = shoulder. [b] Diethyl ether–isopentane–ethyl alcohol (5 : 5 : 2). [c] Very broad bands of which the maximum was not easy to determine. Except for the possibility that these bands could be assigned to the monocarbonyl formed, they might be due to matrix effects.

corresponding to $[Rh(^{12}CO)(^{13}CO)L]$. The observed relative intensities of the two terminal CO bands in a CH_4 matrix, obtained by tracing and weighing bands, were used to calculate a OC–M–CO angle of about 97° (Table 3), using the standard expression[23] $I_{sym}/I_{antisym} = \cot^2(\theta/2)$. The values obtained are in reasonable agreement with the values found for $[Rh(acac)(CO)_2]$ (88.9,[24] 85°[25]) and $[Rh(PhCOCHCOCF_3)(CO)_2]$ (87°)[26] by *X*-ray crystallography.

Irradiation of the matrices using the laser light (351 nm) or the filtered medium-pressure mercury arc (filter A) corresponding to the long-wavelength electronic absorption bands, *e.g.* Figure 2(*a*) and (*b*), Table 2, led to the production of free CO (*ca.* 2 136 cm^{-1}) and a single terminal CO band in each case at *ca.* 2 010 cm^{-1} together with weak visible bands, *e.g.* Figure 2(*c*), Table 2, with corresponding decrease in the parent i.r. and u.v.–visible band intensities. In addition two weaker i.r. bands (*ca.* 2 060 and *ca.* 1 990 cm^{-1}) were also observed [Figure 1(*b*), Table 1], on further photolysis. Irradiation with visible light from the mercury lamp (filter B) corresponding to these new weak visible bands caused new bands to decrease and regenerated the parent bands. The high dilution used in the experiment and the reversibility of the matrix reaction indicates the absence of any polynuclear aggregation. The formation of free CO and the observation of single terminal CO bands (Table 1) suggests that the species responsible for the band at *ca.* 2 010 cm^{-1} are [Rh(CO)L] (see ^{13}CO section). The two weaker bands at *ca.* 2 060 and *ca.* 1 990 cm^{-1} observed on prolonged photolysis in addition to the band of [Rh(CO)L] can be attributed to species in which one end of the bidentate ligand L has become detached. Such species could correspond to the type of short-lived radical intermediates detected in the flash photolysis of *trans*-$[Rh(tfa)_3]$, *i.e.* where one of the tfa ligands has become unidentate.[11,12] Alternatively, the species could correspond to semi-chelated metal-β-diketone complexes having one long and one short M–O bond similar to those found in the complex $[Pd(hfa)_2(Ph_2PC_2H_4PPhC_2H_4PPh_2)]$.[16]

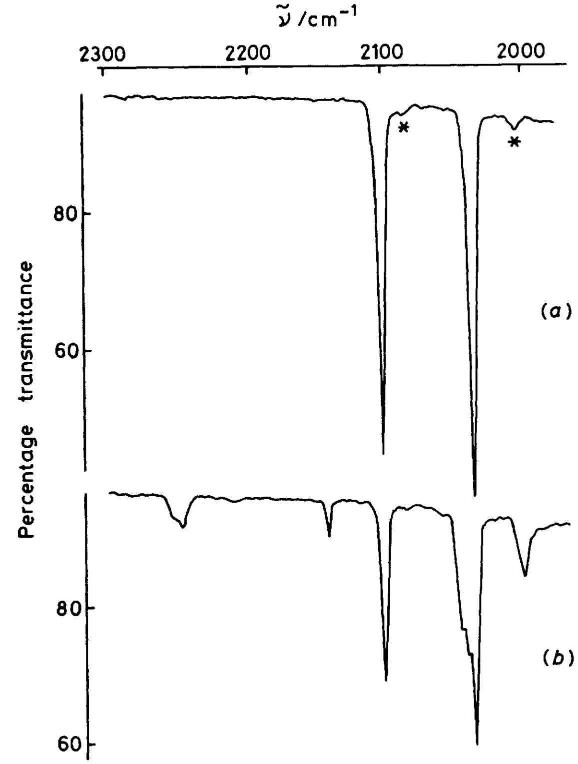


Figure 3. Infrared spectra from an experiment with $[Rh(tfa)(CO)_2]$ isolated at high dilution in a N_2 matrix at 12 K: (*a*) after deposition; (*b*) after photolysis for 5 h using the laser. Bands marked * are due to $[Rh(tfa)(^{12}CO)(^{13}CO)]$ in natural abundance

The photoreactions were observed to be slower in Ar compared to those in CH_4 matrices.[27]

Photolysis of $[Rh(CO)_2L]$ *Complexes in* N_2 *Matrices.*—The i.r. spectra of $[Rh(CO)_2L]$ complexes isolated at high dilution in pure N_2 matrices in the terminal CO-stretching region [Figure 3(*a*), Table 1] are very similar to those in Ar and CH_4 matrices [Figure 1(*a*)]. The two terminal CO-stretching bands correspond to the symmetric and asymmetric (A_1 and B_1 or A' and A'') modes as before. Periods of photolysis using the laser (351 nm) or medium-pressure mercury arc and filter A produced new i.r. bands [Figure 3(*b*)] at *ca.* 2 250, *ca.* 2 136, and *ca.* 2 040 cm^{-1} together with a weak band at *ca.* 2 010 cm^{-1}, of which the second band corresponds to CO liberated by photolysis. In addition to these bands, two bands at *ca.* 2 060 and *ca.* 1 990 cm^{-1} were also observed (Table 1). Irradiation with the visible light from the mercury lamp (filter B) produced slight decreases in bands at *ca.* 2 250 and *ca.* 2 040 cm^{-1} and also decreases in the bands at *ca.* 2 010 cm^{-1}, with increases in the intensities of parent bands.

Taking into account the dilution and the subsequent reversibility of the primary photolysis step, these bands can be assigned to three mononuclear species. The weak bands at *ca.* 2 010 cm^{-1} can be assigned to the terminal CO-stretching mode of [Rh(CO)L] species and the bands at *ca.* 2 060 and *ca.* 1 990 cm^{-1} to the ' unidentate ' $[Rh(CO)_2L]$ species in comparison to those in CH_4 and Ar matrices (Table 1). The bands at *ca.* 2 250 cm^{-1} can be assigned to ^{14}N–^{14}N stretching modes and those at *ca.* 2 040 cm^{-1} to the terminal CO-stretching modes of $[Rh(CO)(N_2)L]$ complexes. The reversibility of the $[Rh(CO)(N_2)L]$ complexes is analogous to the behaviour of $[Fe(\eta^4\text{-}C_4H_4)(CO)_2(N_2)]$[28] and other matrix-isolated dinitrogen complexes, *e.g.* $[Ni(CO)_3(N_2)]$,[29] which have ν(NN) above

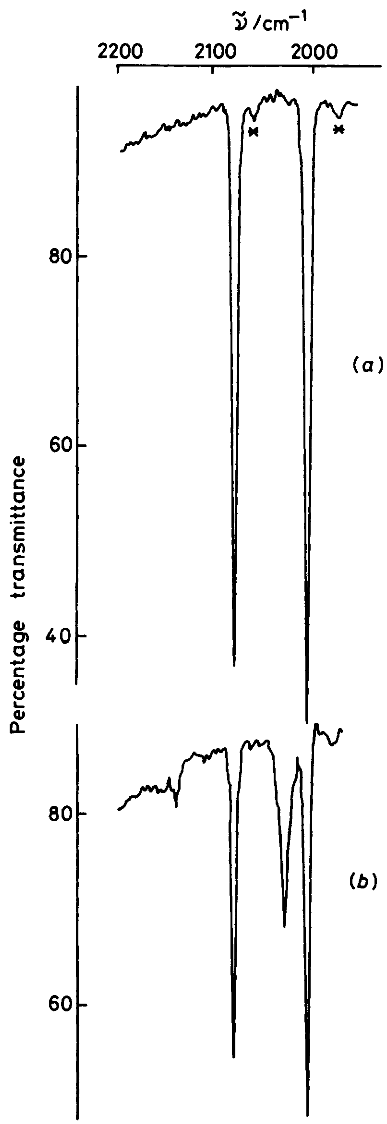


Figure 4. Infrared spectra from an experiment with [Ir(acac)(CO)$_2$] isolated at high dilution in a CH$_4$ matrix at 12 K: (*a*) after deposition; (*b*) after photolysis for 30 min using the unfiltered mercury lamp

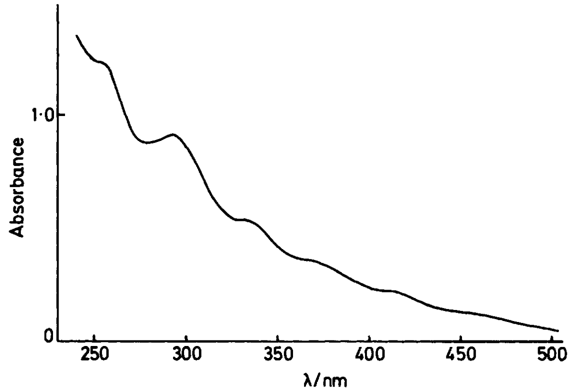


Figure 5. Ultraviolet–visible spectra from an experiment with [Ir(acac)(CO)$_2$] isolated at high dilution in a CH$_4$ matrix at 12 K, after deposition

Table 3. The observed relative intensity of the two terminal CO bands ($I_{sym}/I_{antisym}$) and the calculated OC–M–CO angle (θ) in [M(CO)$_2$L] complexes isolated in a CH$_4$ matrix at 12 K

Complex	$I_{sym}/I_{antisym}$	θ */°
[Rh(acac)(CO)$_2$]	0.794	97
[Rh(tfa)(CO)$_2$]	0.788	97
[Rh(hfa)(CO)$_2$]	0.816	96
[Ir(acac)(CO)$_2$]	0.690	101
[Ir(tfa)(CO)$_2$]	0.760	98

* Accuracy ±1°.

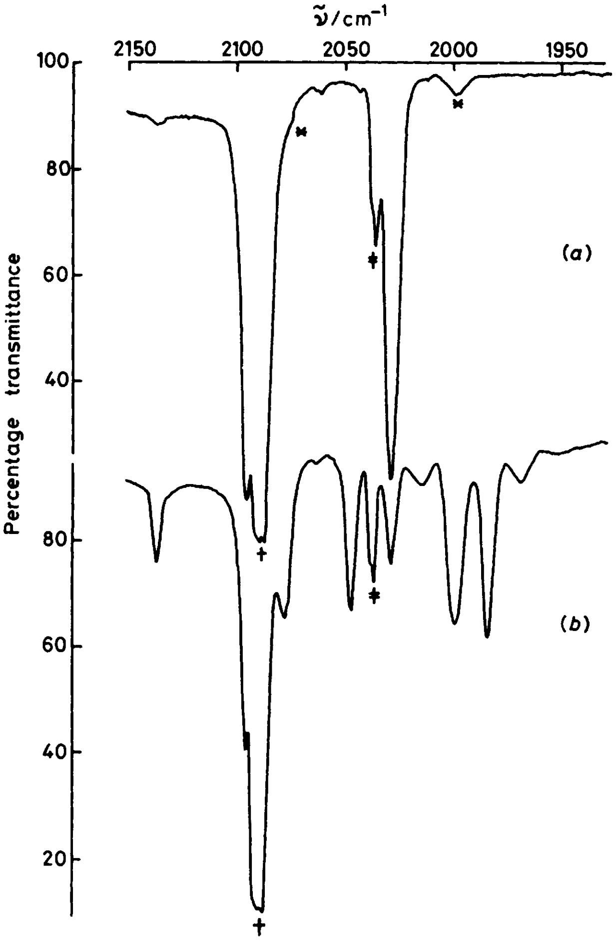


Figure 6. Infrared spectra from an experiment with [Rh(tfa)(CO)$_2$] isolated at high dilution in a ^{13}CO-doped (5%) CH$_4$ matrix at 12 K: (*a*) after deposition and (*b*) after photolysis for 60 min using the mercury arc and filter A. Bands marked * are due to [Rh(tfa)(^{12}CO)(^{13}CO)] in natural abundance, † are due to $^{13}C^{16}O$, and ‡ are due to $^{13}C^{18}O$

2 200 cm^{-1}, and is in contrast to observations for dinitrogen complexes, [Co(η^5-C$_5$H$_5$)(CO)(N$_2$)],[10] [Mn(η^5-C$_5$H$_5$)(CO)$_2$(N$_2$)],[28] and [Mo(η^5-C$_5$H$_5$)(CO)$_2$(N$_2$)(CH$_3$)],[30] which have ν(NN) below 2 200 cm^{-1}.

Photolysis of [Rh(CO)$_2$L] (L = acac *or* tfa) *Complexes in* CO *Matrices.*—The i.r. spectra of [Rh(CO)$_2$L] isolated at high dilution in CO matrices showed two bands similar to those observed for CH$_4$, Ar, and N$_2$ matrices (Table 1). Prolonged photolysis (15 h) with the medium-pressure mercury arc and

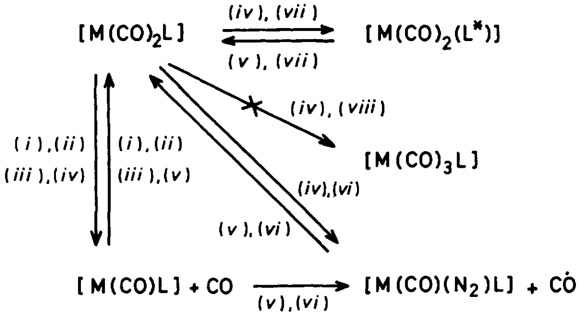
Table 4. Observed and calculated [a] wavenumbers (cm^{-1}) of terminal CO-stretching bands of ^{13}CO-enriched complexes in a CH_4 matrix

Complex	ν_{CO}		Observed	Calculated
[Rh(acac)(^{12}CO)$_2$]	C_{2v}	A_1	2 086.0 [b]	2 085.4
		B_1	2 016.0	2 015.2
[Rh(acac)(^{12}CO)(^{13}CO)]	C_s	A'	2 068.5	2 069.1
		A''	1 985.2	1 986.0
[Rh(acac)(^{13}CO)$_2$]	C_{2v}	A_1	2 040.0 [c]	2 039.1
		B_1	1 970.2	1 970.4
[Rh(tfa)(^{12}CO)$_2$]	C_{2v}	A_1	2 096.0	2 095.3
		B_1	2 029.7	2 029.4
Rh(tfa)(^{12}CO)(^{13}CO)]	C_s	A'	2 078.4	2 079.2
		A''	1 993.3	1 999.6
[Rh(tfa)(^{13}CO)$_2$]	C_{2v}	A_1	2 048.2	2 048.7
		B_1	1 983.9	1 984.3
[Rh(hfa)(^{12}CO)$_2$]	C_{2v}	A_1	2 103.3	2 103.0
		B_1	2 039.2	2 039.0
[Rh(hfa)(^{12}CO)(^{13}CO)]	C_s	A'	*b*	2 087.1
		A''	2 008.9	2 008.9
[Rh(hfa)(^{13}CO)$_2$]	C_{2v}	A_1	2 056.0	2 056.3
		B_1	1 993.5	1 993.7
[Ir(acac)(^{12}CO)$_2$]	C_{2v}	A_1	2 074.1	2 073.8
		B_1	2 000.2	1 999.4
[Ir(acac)(^{12}CO)(^{13}CO)]	C_s	A'	2 056.6	2 057.2
		A''	1 969.8	1 970.8
[Ir(acac)(^{13}CO)$_2$]	C_{2v}	A_1	2 026.8	2 027.7
		B_1	1 954.3	1 955.0
[Ir(tfa)(^{12}CO)$_2$]	C_{2v}	A_1	2 083.1 [b]	2 082.2
		B_1	2 011.5	2 010.7
[Ir(tfa)(^{12}CO)(^{13}CO)]	C_s	A'	2 064.8	2 065.7
		A''	1 980.9	1 981.7
[Ir(tfa)(^{13}CO)$_2$]	C_{2v}	A_1	*c*	2 035.9
		B_1	1 965.7	1 966.0
[Rh(acac)(^{12}CO)]	A'		2 001.8	
[Rh(acac)(^{13}CO)]	A'		1 955.7	1 955.8
[Rh(tfa)(^{12}CO)]	A'		2 015.4	
[Rh(tfa)(^{13}CO)]	A'		1 969.1	1 969.1
[Rh(hfa)(^{12}CO)]	A'		2 027.9	
[Rh(hfa)(^{13}CO)]	A'		1 980.8	1 981.3
[Ir(acac)(^{12}CO)]	A'		2 032.0 [c]	
[Ir(acac)(^{13}CO)]	A'		1 985.7	1 985.3
[Ir(tfa)(^{12}CO)]	A'		2 037.9 [c]	
[Ir(tfa)(^{13}CO)]	A'		1 991.4	1 991.0

[a] For [Rh(acac)(CO)$_2$], K = 1 698.8 and k_1 = 58.2; [Rh(tfa)(CO)$_2$], K = 1 718.7 and k_1 = 54.9; [Rh(hfa)(CO)$_2$], K = 1 733.2 and k_1 = 53.6; [Ir(acac)(CO)$_2$], K = 1 676.3 and k_1 = 61.2; [Ir(tfa)(CO)$_2$], K = 1 692.5 and k_1 = 59.1 N m^{-1}; [Rh(acac)(CO)], K_{CO} = 1 618.2; [Rh(tfa)(CO)], K_{CO} = 1 640.3; [Rh(hfa)(CO)], K_{CO} = 1 660.7; [Ir(acac)(CO)], K_{CO} = 1 656.8; [Ir(tfa)(CO)], K_{CO} = 1 677.1 N m^{-1}. [b] Band obscured by matrix $^{13}C^{16}O$ bands. [c] Band obscured by matrix $^{13}C^{18}O$ bands.

filter A resulted in the production of the monocarbonyl only in the case of [Rh(tfa)(CO)$_2$] (band at *ca.* 2 012 cm^{-1}), similar to Ar, CH_4, and N_2 matrices, while no new i.r. bands were observed for the [Rh(acac)(CO)$_2$] complex. Interestingly no evidence was found for the formation of an expanded-co-ordination-number species such as [Rh(CO)$_3$L] in the CO matrix. This is in contrast to the results observed for two other dicarbonyl species, [Co(η^5-C_5H_5)(CO)$_2$] [10] and [Fe(η^5-C_5H_5)(CO)$_2$(CH_3)],[31] which give [Co(η^3-C_5H_5)(CO)$_3$] and [Fe(η^3-C_5H_5)(CO)$_3$(CH_3)] respectively.

Photolysis of [Ir(CO)$_2$L] (L = acac *or* tfa) *Complexes in* CH_4 *Matrices.**—The spectra of [Ir(CO)$_2$L] complexes isolated at high dilution in CH_4 matrices showed multiply split symmetric and asymmetric terminal CO-stretching bands [Figure 4(*a*), Table 1], as observed in the case of the corresponding rhodium complexes. The observed relative intensities of the two terminal CO bands yielded an OC–M–CO angle of *ca.* 99° in these complexes (Table 3).



Scheme. L* = Unidentate L. (*i*) CH_4 or Ar, M = Rh, L = acac, tfa, or hfa; (*ii*) N_2 or CO, M = Rh, L = tfa; (*iii*) CH_4, M = Ir, L = acac or tfa, filter C or unfiltered; (*iv*) filter A or laser; (*v*) filter B; (*vi*) N_2, M = Rh, L = acac, tfa, or hfa; (*vii*) CH_4, Ar, or N_2, M = Rh, L = acac, tfa, or hfa; (*viii*) CO, M = Rh, L = acac, tfa, or hfa

Irradiation of the matrices with the medium-pressure mercury arc corresponding to excitation of a number of electronic transitions, *e.g.* Figure 5 and Table 2 (filter C or unfiltered), led to the production of a band of free CO (*ca.* 2 136 cm^{-1}) and bands at *ca.* 2 030 cm^{-1} only [Figure 4(*b*)]. These single bands can be assigned to the [Ir(CO)L] species in comparison with similar observations for the rhodium complexes.

Photolysis of [M(CO)$_2$L] *Complexes in* ^{13}CO-*doped* (5%) *Methane Matrices.*—The i.r. spectra of [M(CO)$_2$L] complexes isolated at high dilution in ^{13}CO doped (5%) CH_4 matrices [Figure 6(*a*)] show two strong symmetric and asymmetric bands of the di-^{12}CO species together with two weak bands (marked with an asterisk) corresponding to the natural-abundance amounts of [M(^{12}CO)(^{13}CO)L] complexes.

Irradiation of the matrices with the medium-pressure mercury arc and filter A caused rapid growth of the bands corresponding to [M(^{12}CO)(^{13}CO)L] and [M(^{13}CO)$_2$L] [Figure 6(*b*)], as confirmed by the excellent agreement between the observed and calculated [10,23] band positions (Table 4) for a C_{2v}–M(CO)$_2$ fragment. Further photolysis of these complexes gave the ^{13}CO-enriched product bands corresponding to the ^{12}CO bands previously assigned to monocarbonyl species. In these cases too, the good correspondence between the observed and calculated band positions (Table 4) of the M(CO) fragment confirms the assignment of the bands to [M(CO)L] species.

Due to the low conversion into the other species it was not possible, using ^{13}CO force-field fitting, to confirm their assignment as 'unidentate' [M(CO)$_2$L] species (see Discussion).

Discussion

The photoreactions of [M(CO)$_2$L] complexes at high dilution in various matrices are summarised in the Scheme.

The observation of co-ordinatively unsaturated monocarbonyl species, [M(CO)L], even in CO matrices, is consistent with a dissociative mechanism for the ligand-exchange and substitution reactions of [M(CO)$_2$L] complexes. In all the complexes studied, varying the electronic structure of ligand L

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* Due to the extremely low photoreactivity of iridium complexes in Ar matrices, data are only reported for CH_4 matrix experiments.

from acac to hfa and varying the metal resulted in spectra which demonstrate that the dissociation of CO is the primary photochemical reaction. That is, the hitherto neglected dissociative pathway is probably important for the exchange reactions of these 16-electron complexes. This is in contrast to the S_N2 associative mechanism proposed for the corresponding $[M(C_2H_4)_2L]$ complexes.[2-4] The following order of reactivities is noted in the complexes studied: (*i*) for a given metal, hfa > tfa > acac; and (*ii*) for a given ligand, Rh > Ir.

The order of reactivity could be related to the electronic properties of the β-diketonate ligand. In going from acac to tfa to hfa, the CH_3 groups in the diketone are substituted by the more electron-withdrawing CF_3 groups and hence the M–CO bond strengths in the $[M(CO)_2L]$ complexes will follow the order L = acac > tfa > hfa. This is reflected in the increases of observed i.r. frequencies of the parent complexes (Table 1, acac < tfa < hfa) and in the increase in values of the CO-stretching force constants, *K* (Table 4).

The influence of the β-diketone ligands in the complexes $[M(olefin)_2L]$ has been studied using vibrational and n.m.r. spectroscopy and it has been reported that the metal-to-olefin π backbonding decreases in the order acac > tfa > hfa.[22,32] In the case of non-symmetrical β-diketones such as thienyltrifluoroacetylacetonate[33] and $PhCOCHCOCF_3$,[26] *cf.* tfa, it has been shown that the carbonyl group *cis* to the oxygen atom nearest to the CF_3 group is displaced. This is in agreement with the polarisation theory,[34] where the oxygen atom nearest to the CF_3 group will be least polarisable as a result of the electron-attracting power of the CF_3 group. The increased reactivity of rhodium compared to iridium complexes could be due to the increased π backbonding and higher σ-bonding capacity of iridium when compared with that of rhodium.[32] This higher σ-bonding capability of iridium is also observed for the M–P σ bond in the photoelectron spectra of $[MH(PF_3)_4]$ (M = Rh or Ir) complexes.[35]

In CO matrices, no evidence was obtained for the formation of expanded-co-ordination-number species, $[M(CO)_3L]$ (M = Rh), in contrast to the expanded-co-ordination-number species $[Co(\eta^3\text{-}C_5H_5)(CO)_3]$[10] and $[Fe(\eta^3\text{-}C_5H_5)(CO)_3(CH_3)]$[31] produced from the complexes $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ respectively.

Conclusive assignments for the 'unidentate' $[M(CO)_2L^*]$ (M = Rh) complexes observed on photolysis of $[M(CO)_2L]$ can only be made using a signal-averaging multiple scanning and averaging i.r. spectrometer. Future work, using a Nicolet 7199 FTIR spectrometer, will seek to find the acetylacetonate CO vibration of the intermediate species in order to determine the nature of bonding in the acetylacetonate ligand.

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