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Photochemistry of Dicarbonyl(1,1,1-trifluoroacetylacetonato-)rhodium [(tfa)Rh(CO)$_2$] in Frozen Gas Matrices at 12 K

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Early studies of the ligand exchange reactions of 16 electron four coordinate compounds, *e.g.* (acac)Rh(C_2H_4)$_2$ (acac = acetylacetonate), showed that these reacted in solution by a S_N2 associative mechanism [1]. However the 18 electron compounds of Rh and Co, *e.g.* (η^5-C_5H_5–Rh(C_2H_4)$_2$ [1] and (η^5-C_5H_5)Co(CO)$_2$ [2], behaved differently and a dissociative S_N1 mechanism has been suggested for their solution exchange reactions. Though no evidence has been found for the formation of (η^5-C_5H_5)-Co(CO) and CO on photolysis of (η^5-C_5H_5)Co(CO)$_2$ in a gas matrix at 12 K, the existence of an equilibrium involving an associative reaction

$$(\eta^5\text{-}C_5H_5)Cl(CO)_2 + CO \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} (\eta^3\text{-}C_5H_5)Co(CO)_3$$

has been demonstrated [3]. A flash photolysis study [4] of *trans*-(tfa)$_3$Rh showed the existence of a short-lived radical species as the intermediate in both isomerisation and decomposition reactions but could not provide any structural information for the species. In order to investigate unstable species in the chemistry of rhodium and iridium, we have undertaken a study of the complexes (R ~ R')ML$_2$ (R ~ R' = acac, tfa, hfa; M = Rh, Ir; L = C_2H_4, CO) in inert (Ar, CH_4) and reactive (CO, N_2) gas matrices at 12 K. We report here the results for (tfa)Rh(CO)$_2$ which indicate that the hitherto neglected dissociative path may be important in the exchange reactions of 16 electron complexes.

Experimental

Cryogenic temperatures (*ca.* 12 K) were obtained using a closed cycle liquid helium refrigerator (Air Products and Chemicals Inc., CSA-202). Matrices (complex: host matrix ~1:2000) were prepared by the slow spray-on method [3], where the vapour from the sample (held at 10 °C) was co-condensed with excess matrix gas on to the cold spectroscopic window. Infrared spectra were recorded on a Grubb Parsons Spectromajor spectrometer. Wavelength-selective photolysis was achieved using a Phillips HPK 125-W medium pressure mercury lamp in conjunction wih combinations of absorbing materials: $310 < \lambda < 380$ nm – pyrex disc (thickness 5 mm) + quartz gas cell (pathlength 25 mm) containing Br_2 (200 torr); $\lambda < 280$ and $\lambda > 550$ nm – two quartz gas cells (pathlength 25 mm) containing Cl_2 (2 atm.) and Br_2 (200 torr); $\lambda > 410$ nm – Corning glass filter (C.S. 3-74). Matrix gases (Ar, CH_4, CO, and N_2) were of grade 'X' purity and obtained from B.O.C. Ltd. (tfa)Rh(CO)$_2$ was purified by sublimation and the

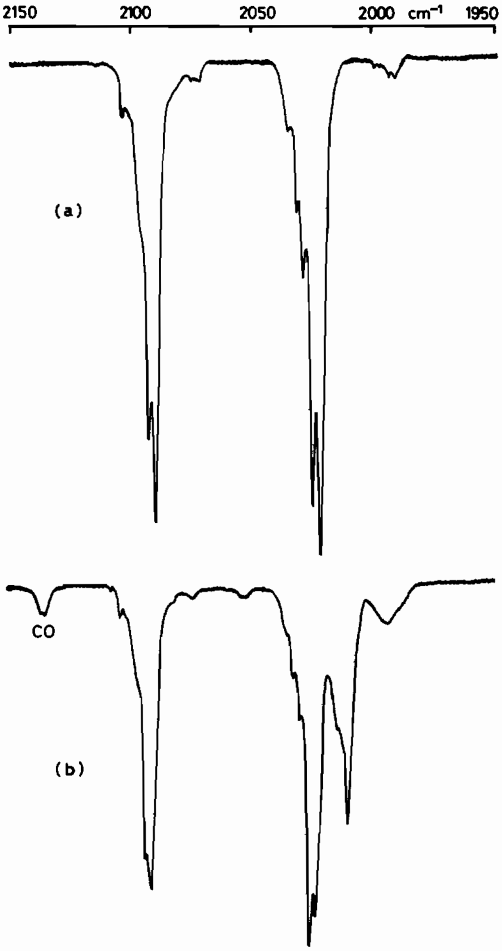

Fig. 1. Infrared spectra from an experiment with (tfa)Rh-(CO)$_2$ isolated in a CH_4 matrix at 12 K: (a) after deposition and (b) after ultraviolet irradiation for 75 min.

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TABLE I. Infrared Band Positions (cm^{-1}) for $(tfa)Rh(CO)_2$ and its Photoproducts in Gas Matrices at 12 K in the CO Stretching Region.

Compound	CH_4	Ar	CO	N_2
$(tra)Rh(CO)_2$	2094.3 2028.1	2094.8 2028.0	2097.2 2031.9	2100.0 2034.0
(tfa)Rh(CO)	2013.7	$\left.\begin{matrix}2016.0\\2013.0\end{matrix}\right\}^{a}$	2012.0^{b}	2019.6
$(tfa)Rh(CO)(N_2)$				2248.0 (ν_{N_2}) 2041.7 (ν_{CO})
$(\eta^1\text{-tfa})Rh(CO)_2$	2055.8 1996.7	2054.7 1998.0	c	2058.2 1998.3

[a] Matrix splitting. [b] Long photolysis time (15 hours) required. [c] Not detected.

purity was checked by elemental analysis, infrared and NMR spectroscopy. ^{13}CO (95%) was obtained from B.O.C. Prochem.

Results and Discussion

The infrared spectrum of $(tfa)Rh(CO)_2$ isolated in a CH_4 matrix is shown in Fig. 1(a). The two terminal CO stretching bands (2091.3 and 2028.1 cm^{-1}) correspond to the A_1 and B_1 modes expected for a molecule with C_{2v} local symmetry for the CO ligands. Irradiation of the matrix with the filtered medium pressure mercury are ($310 < \lambda < 380$ nm and/or $\lambda < 280$ and $\lambda > 550$ nm) produced the spectrum shown in Fig. 1(b). Destruction of the parent molecule is accompanied by the growth of an intense new band (2013.7 cm^{-1}), weaker bands (2055.8 and 1996.7 cm^{-1}) and a band corresponding to free CO (2136.0 cm^{-1}). Irradiation with the visible region output of the mercury lamp ($\lambda > 410$ nm) caused the new bands to decrease and regenerated the parent bands. The dilution used (*ca.* 1:2000) and the reversibility of the matrix reaction indicates the absence of any polynuclear aggregation. The formation of free CO (Fig. 1(b)) and the observation of a single strong band in CH_4, Ar and CO matrices (Table I) suggests that the species responsible for the 2015 cm^{-1} band is (tfa)Rh(CO). This is supported by ^{13}CO labelling studies (5% ^{13}CO in CH_4) when a strong new band was observed at 1968.9 cm^{-1} which is in excellent agreement with the calculated position (1969.7 cm^{-1}) for a monocarbonyl species. Ultraviolet irradiation of $(tfa)Rh(CO)_2$ isolated at high dilution in a N_2 matrix gave new product bands at 2248.0 and 2041.7 cm^{-1} together with a band due to free CO. Taking into account the dilution and the subsequent reversibility of the primary photolysis step, these bands can also be assigned to a mononuclear species. The band at 2248.0 cm^{-1} can be assigned to a NN stretching vibration [3] and the band at 2041.7 cm^{-1} can be assigned to the terminal CO stretching vibration of $(tfa)Rh(CO)(N_2)$.

Prolonged photolysis of $(tfa)Rh(CO)_2$ in Ar, CH_4, and N_2 matrices showed the growth of two weaker bands (2055 and 1977 cm^{-1}, Table I) in addition to the band of (tfa)Rh(CO). The two weaker bands were not observed on prolonged photolysis in the CO matrices. We attribute the two weaker bands to a species in which one end of the bidentate tfa ligand has become detached, *i.e.* $(\eta^1\text{-tfa})Rh(CO)_2$. It is possible that this species corresponds to the short-lived radical detected in the flash photolysis of $(tfa)_3Rh$ [4].

The observation of the monocarbonyl species (tfa)Rh(CO) is consistent with a dissociative mechanism for the ligand exchange and substitution reactions of $(tfa)Rh(CO)_2$. Interestingly no evidence was found for the formation of an expanded co-ordination number species such as $(tfa)Rh(CO)_3$ in CO matrix experiments. This is in contrast to the results for $(\eta^5\text{-}C_5H_5\text{–}Co(CO)_2$ [3] described above. Further studies with other 16 electron compounds will be carried out to confirm whether co-ordinatively unsaturated species could be possible intermediates in their ligand exchange and substitution reactions. Additionally the role of electronic configurations and of excited states in the photochemical reactions of a series of analogous $(R \sim R')ML_2$ complexes of Rh and Ir will be investigated and compared with the results obtained from photoelectron spectroscopy [5].

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