

### Preliminary communication

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## DIRECT INFRARED SPECTROSCOPIC EVIDENCE FOR THE EJECTION OF VINYL CHLORIDE ON PHOTOLYSIS OF RHODIUM-(ACETYLACETONATE)BIS(VINYL CHLORIDE) IN FROZEN GAS MATRICES AT 12 K

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### Summary

Infrared spectroscopic studies using  $\text{Rh}(\text{acac})\text{L}_2$  (acac = acetylacetonate; L =  $\text{CH}_2=\text{CHCl}$ ,  $\text{CH}_2=\text{CHMe}$ ) complexes have demonstrated for the first time that  $\nu(\text{C}=\text{C})$  can be used to characterise unstable species in matrix isolation experiments on metal-olefin complexes at ca. 12 K provided that the olefin is asymmetric such that  $\nu(\text{C}=\text{C})$  is a relatively high intensity mode in both the metal complexes and the "free" ligand.

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Photosubstitution reactions of complexes of the type  $\text{M}(\beta\text{-diketonate})\text{LL}'$  (M = Rh, Ir; L, L' = CO,  $\text{PPh}_3$ ,  $\text{AsPh}_3$ , olefin) have been the subjects of a number of recent papers. These complexes react differently under various circumstances. For example, the complexes  $\text{M}(\text{acac})(\eta^2\text{-C}_2\text{H}_4)_2$  (M = Rh, Ir; acac = acetylacetonate) have been shown to react in solution by  $\text{S}_{\text{N}}2$  associative mechanisms [1], while for  $\text{M}(\beta\text{-diketonate})(\text{CO})_2$  (M = Rh, Ir) complexes  $\text{S}_{\text{N}}1$  dissociative pathways have been proposed [2].

Flash photolysis studies point to the existence of short-lived radical species in both isomerisation and substitution reactions [3]. Although no firm structural evidence was presented, it was suggested that the primary process was cleavage of a metal- $\beta$ -diketonate bond [3, 4]. Matrix isolation studies for  $\text{M}(\beta\text{-diketonate})(\text{CO})_2$  complexes in frozen gas matrices at ca. 12 K observed CO loss and, to a lesser extent, metal- $\beta$ -diketonate bond cleavage [2].

Matrix isolation studies of organometallic complexes have primarily used

metal carbonyl IR active stretching bands to characterise unstable species [5]. This is because other metal–ligand vibrations and internal ligand vibrations are relatively weak or do not show sufficiently characteristic shifts to allow characterisation of unstable species. For example, ca.  $30\text{ cm}^{-1}$  shifts were observed in  $\nu(\text{CO})$  for  $\text{M}(\beta\text{-diketonate})(\text{CO})$  versus  $\text{M}(\beta\text{-diketonate})(\text{CO})_2$  complexes whereas no apparent shifts could be detected for the vibrations of the  $\text{M}(\beta\text{-diketonate})$  fragment under the same circumstances [2, 6]. In a comparable matrix isolation study of  $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$ , reversible loss of  $\text{C}_2\text{H}_4$  was claimed to occur but no definitive proof was presented because  $\nu(\text{C}=\text{C})$  is infrared inactive in “free”  $\text{C}_2\text{H}_4$  and is at best very weak in  $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2$  [7].

In this communication we demonstrate that matrix isolation studies\* of olefin complexes can employ  $\nu(\text{C}=\text{C})$  for characterisation if the olefin is rendered asymmetric by substituting a H by a Me or a Cl ligand.

Isolation of  $\text{Rh}(\text{acac})(\eta^2\text{-CH}_2=\text{CHCl})_2$  in 5% CO doped  $\text{CH}_4$  matrices at high dilution (ca. 1/2000) at 12 K affords well resolved bands in the terminal CO stretching region (Fig. 1 and 2) and ligand vibration regions (Fig. 2). Irradiation of the matrices with UV light ( $\lambda < 280\text{ nm}$  and  $\lambda > 550\text{ nm}$ ) caused dramatic changes in the terminal CO region associated with the ejection of  $\text{CH}_2=\text{CHCl}$  and the formation of  $\text{Rh}(\text{acac})(\text{CO})(\eta^2\text{-CH}_2=\text{CHCl})$  and  $\text{Rh}(\text{acac})(\text{CO})_2$  (Table 1). Changes in the region associated with the ligands are less marked although after 90 min photolysis a new band can be clearly observed at  $1606\text{ cm}^{-1}$  (band marked \* in Fig. 2). This band was positively identified as “free”  $\text{CH}_2=\text{CHCl}$  from

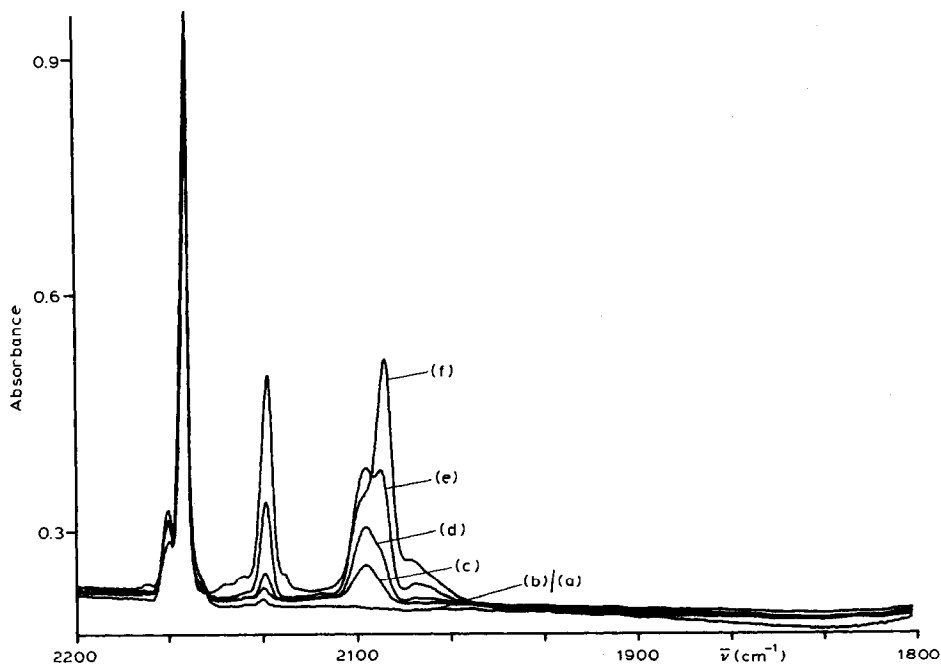


Fig. 1. IR spectra (Nicolet 7199 FTIR interferometer ( $1\text{ cm}^{-1}$  resolution) in the terminal  $\nu(\text{CO})$  region from an experiment with  $\text{Rh}(\text{acac})(\eta^2\text{-CH}_2=\text{CHCl})_2$  in a 5% CO doped  $\text{CH}_4$  matrix at 12 K: (a) before irradiation, (b) after 10 min photolysis, (c) after 90 min photolysis, (d) after 3 h photolysis, (e) after 10 h photolysis and (f) after 30 h photolysis.

\*See ref. 2 for details of matrix isolation equipment, the photolysis source and wavelength selective filters.

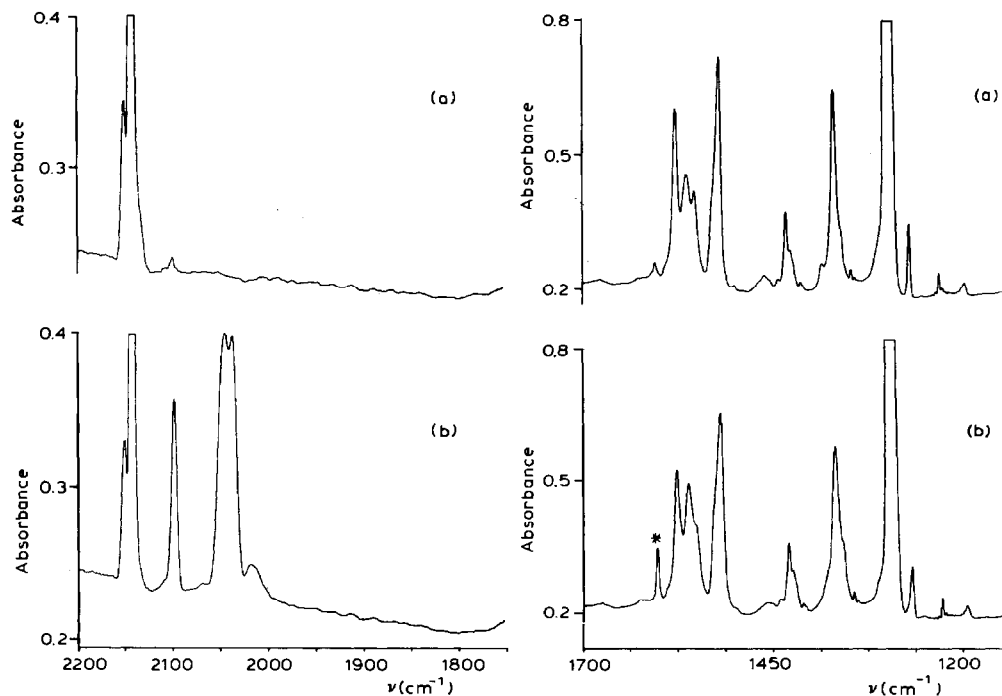


Fig. 2. IR spectra in both terminal  $\nu(\text{CO})$  and ligand vibration region experiments: (a) after deposition and (b) after 90 min photolysis. The band marked \* is  $\nu(\text{C}=\text{C})$  for "free"  $\text{CH}_2=\text{CHCl}$ .

TABLE 1

INFRARED BAND POSITIONS ( $\text{cm}^{-1}$ ) OF  $\text{CH}_2=\text{CHCl}_2$ ,  $\text{Rh}(\text{acac})(\text{CO})_2$ ,  $\text{Rh}(\text{acac})(\eta^2\text{-CH}_2=\text{CHCl})_2$  AND ITS PHOTOPRODUCTS IN EXPERIMENTS EMPLOYING 5% CO DOPED  $\text{CH}_4$  MATRICES AT 12 K

Experiment <sup>a</sup>						Band, assignment
A	B	C	D	E	F	
		2087.9	2086.7			} $\nu(\text{CO})$
	2028.1	2019.6	2015.0			
		1605.8		1605.8	1607.0	} $\nu(\text{C}=\text{C})$ for "free" $\text{CH}_2=\text{CHCl}_2$
1579.4						
	1565.2					} bands for bound $\text{CH}_2=\text{CHCl}$ and acetylacetonate
1522.2						
1435.0	1435.0	1433.7	1438.5			} bands for bound $\text{CH}_2=\text{CHCl}$ and acetylacetonate
			1425.2			
1372.4	1372.4	1373.1	1377.4			} band of $\text{CH}_2=\text{CHCl}$
		1362.6	1363.7	1363.8	1365.5	
1273.4	1273.4	1276.8	1278.5	1281.6	1281.8	band of $\text{CH}_2=\text{CHCl}$
1031.0	1031.0	1031.1	1033.4			} band of $\text{CH}_2=\text{CHCl}$
				1029.0	1027.0	
1022.0	1022.0	1022.0	1020.2			} band of $\text{CH}_2=\text{CHCl}$
		955.3	949.2	955.3	943.7	
898.8	898.8	898.7		899.3	899.6	band of $\text{CH}_2=\text{CHCl}$
		703.5	703.5	707.0	710.7	band of $\text{CH}_2=\text{CHCl}$
684.0	684.0	684.0	683.3			} bands of bound acetylacetonate and M-CO
		629.1	629.0			
615.6	615.6	615.6				

<sup>a</sup> A = after deposition; B = after 10 min photolysis;

C = after 90 min photolysis; D = pure  $\text{Rh}(\text{acac})(\text{CO})_2$ , in a 5% CO doped  $\text{CH}_4$  matrix.

E = subtraction spectrum for lower wavenumber region; F = pure  $\text{CH}_2=\text{CHCl}$ , in a 5%  $\text{CH}_4$  matrix.

separate experiments (Table 1). On careful expansion and subtraction of spectra, the other stronger bands of  $\text{CH}_2=\text{CHCl}$  were detected for the experiments with  $\text{Rh}(\text{acac})(\eta^2\text{-CH}_2=\text{CHCl})_2$  in CO doped  $\text{CH}_4$  matrices (Table 1). Definitive identification of  $\text{Rh}(\text{acac})(\text{CO})_2$  was also afforded by a separate experiment (Table 1).

The stepwise formation of "Rh(CO)" and "Rh(CO)<sub>2</sub>" fragments and the growth of for "free"  $\text{CH}_2=\text{CHCl}$  indicates that first one and then the other  $\text{CH}_2=\text{CHCl}$  ligands are lost, giving the coordinatively saturated 16-electron species  $\text{Rh}(\text{acac})(\text{CO})(\eta^2\text{-CH}_2=\text{CHCl})$  and  $\text{Rh}(\text{acac})(\text{CO})_2$  rather than the formation of the coordinatively unsaturated 14-electron species  $\text{Rh}(\text{acac})(\text{CO})$ . The latter can be eliminated because the band position in this work for "Rh(CO)" (2028  $\text{cm}^{-1}$ ) does not correspond with that for  $\text{Rh}(\text{acac})(\text{CO})$  generated in a pure  $\text{CH}_4$  matrix (2002.9  $\text{cm}^{-1}$ ) [2].

Similar observations were obtained in experiments starting from the propene complex  $\text{Rh}(\text{acac})(\eta^2\text{-CH}_2=\text{CHMe})_2$ . It is apparent, therefore, that creation of asymmetry in olefins will allow feasible characterisation of unstable olefin-containing organometallic species. Further work will seek to establish whether  $\text{Rh}(\text{acac})(\eta^2\text{-CH}_2=\text{CHCl})_2$  affords  $\text{Rh}(\text{acac})(\eta^2\text{-CH}_2=\text{CHCl}) + \text{CH}_2=\text{CHCl}$  reversibly in non-reactive matrices (Ar),  $\text{Rh}(\text{acac})(\text{N}_2)(\eta^2\text{-CH}_2=\text{CHCl})$  in  $\text{N}_2$  matrices and will seek to extend the concept to acetylene complexes using  $\nu(\text{C}\equiv\text{C})$  of  $\text{MeC}\equiv\text{CH}$ ,  $\text{CF}_3\text{C}\equiv\text{CH}$  and  $\text{PhC}\equiv\text{CH}$ .

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