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HIGH PRESSURE INFRARED SPECTROSCOPIC STUDIES OF CARBONYLATION REACTIONS OF OLEFINS IN THE PRESENCE OF GROUP VIIIB METAL CARBONYLS*

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The combination of kinetic measurements, studies of stoichiometric reactions under ambient conditions [1], and our recent IR spectral investigations under actual reaction conditions [2] have produced a generally agreed picture concerning the mechanism of the cobalt carbonyl-catalysed hydroformylation of olefins, indicated in Reaction Scheme 1. However, there are still two basic questions which remain to be answered concerning the general catalysis of the reaction by Group VIIIB metal carbonyl derivatives. Firstly, according to Falbe [1], final proof for the formation of the initial π-complexes and the alkylcobalt carbonyl compounds which are believed to be formed from the π-complexes (steps 2 and 3 of the reaction sequence) under the conditions of the catalytic reaction is still lacking and secondly, there remains, particularly with rhodium and iridium carbonyls, the possible involvement of polynuclear rather than mononuclear species in the reaction cycle. Indeed, the isolation of the anion $[Rh_6(CO)_{15}COR]^-$, where R = Et or Pr, from the stoichiometric hydroformylation of ethylene or propylene respectively in the presence of $Rh_4(CO)_{12}$, under mild conditions, may imply the direct involvement of polynuclear rhodium carbonyl-containing species [3]. Some results, relevant to both these questions,

$$Co_2(CO)_6L_2 + H_2 \rightleftharpoons 2HCo(CO)_3L \rightleftharpoons 2HCo(CO)_2L + 2CO \quad (1)$$

$$HCo(CO)_xL + RCH{=}CH_2 \rightleftharpoons H(RCH{=}CH_2)Co(CO)_xL \quad (2)$$

$$H(RCH{=}CH_2)Co(CO)_xL \rightleftharpoons RCH_2CH_2Co(CO)_xL \quad (3)$$

$$RCH_2CH_2Co(CO)_xL + CO \rightleftharpoons RCH_2CH_2COCo(CO)_xL \quad (4)$$

$$RCH_2CH_2COCo(CO)_xL + H_2 \rightarrow RCH_2CH_2CHO + HCo(CO)_xL \quad (5)$$

$(L = CO \text{ or } PR_3,\ x = 2 \text{ or } 3)$

Scheme 1. Hydroformylation reaction mechanism.

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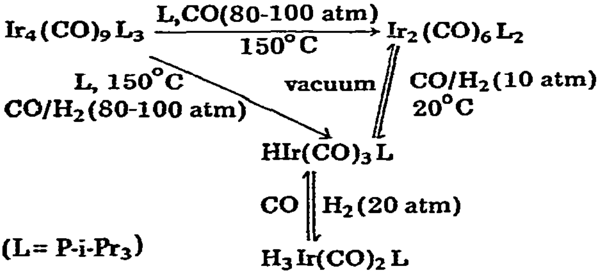
[*] Presented at the Symposium on Metal Carbonyl Chemistry, dedicated to Professor Walter Hieber, held at Ettal (West Germany), July 21st-July 27th, 1974.

which we have obtained from the reactions of an iridium carbonyl system are presented in this paper.

With respect to the first point, one possible reason for the difficulty in observing the direct reaction of an olefin with the hydrido species under hydroformylation conditions lies in the equilibrium position of the first step in the reaction scheme. We have previously shown that, for L = CO or PBu_3, the equilibria lie predominantly on the side of the hydridocarbonyls only at high temperature and pressure. Under conditions where direct addition of the olefin to form the alkyl might be expected to be observed, i.e. the addition of an excess of olefin to the hydride, such treatment results in a shift of the equilibrium to the left hand side, causing a spectrally complicated situation. Ideally what is required is a carbonyl hydride which exists as a single, stable species and which displays a simple infrared spectrum so that small spectral changes may be readily monitored.

In the course of some previous work on the reactions of polynuclear phosphine-substituted iridium carbonyls with CO/H_2 we came across a relatively stable hydrido species $HIr(CO)_3P\text{-i-}Pr_3$ which seemed to fit the above requirements and so be a good example for studying the proposed hydroformylation sequence [4]. This hydrido carbonyl can be obtained as indicated in Reaction Scheme 2. The ready breakdown of the tetranuclear complex under pressure implies that, in this system at least, the hydroformylation reaction should involve catalysis by mononuclear species.



Scheme 2. Preparation of $HIr(CO)_3P\text{-i-}Pr_3$.

The monomeric species is, as expected, a hydroformylation catalyst and infrared spectral changes which are observed during the hydroformylation of hept-1-ene in the presence of $HIr(CO)_3P\text{-i-}Pr_3$ are illustrated in Fig. 1 (the peaks identified by crosses are hept-1-ene absorptions). The spectrum of $HIr(CO)_3P\text{-i-}Pr_3$ alone is observed throughout the reaction, suggesting that, as in the case of the $Co_2(CO)_8/PBu_3$ catalyst system [2], initial addition of the olefin to $HIr(CO)_3P\text{-i-}Pr_3$ is the rate-determining step in the reaction.

Because of the apparent stability of the species $HIr(CO)_3P\text{-i-}Pr_3$ at relatively low pressures and temperatures we decided to study the reactions of the complex with individual gases, namely ethylene, carbon monoxide, and hydrogen, to check for the formation of the expected alkyl, acyl and hydride respectively in the proposed catalytic cycle.

Spectral changes observed when a heptane solution of $HIr(CO)_3P\text{-i-}Pr_3$ is treated with 200 psi ethylene at 50°C are illustrated in Fig. 2. These show the

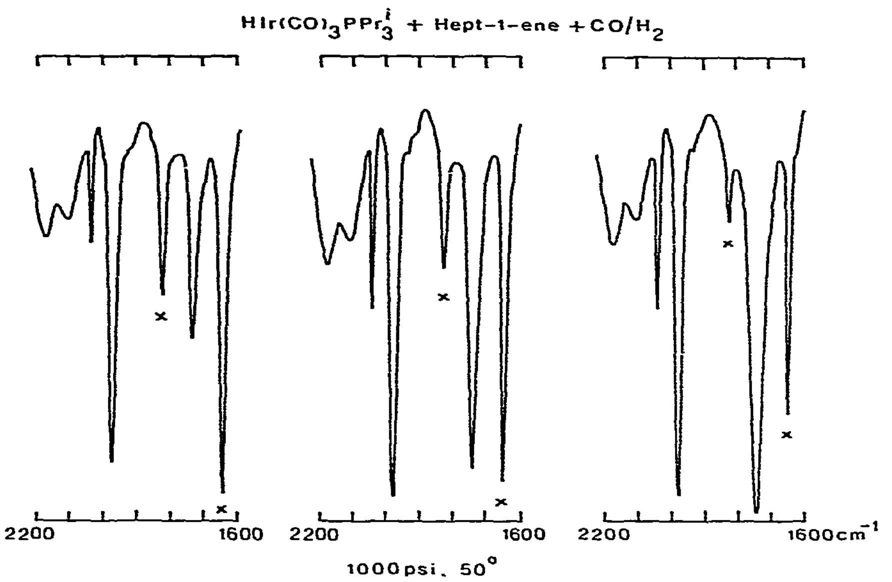


Fig. 1. IR spectral changes during hydroformylation of hept-1-ene in the presence of $HIr(CO)_3P$-i-Pr_3.

appearance of new bands in the ν(CO) region of the spectrum, specifically strong and weak doublets at 1957, 1954 and 2030, 2025 cm^{-1} respectively which increase in intensity as the absorptions at 1970 and 2038 cm^{-1} due to the starting $HIr(CO)_3P$-i-Pr_3 decrease. The weak peak at 1880 cm^{-1} is due to dissolved ethylene. The reaction is complete within ca. 30 min although on standing two additional bands are observed at 2035 and 1974 cm^{-1} (see later). The spectrum ob-

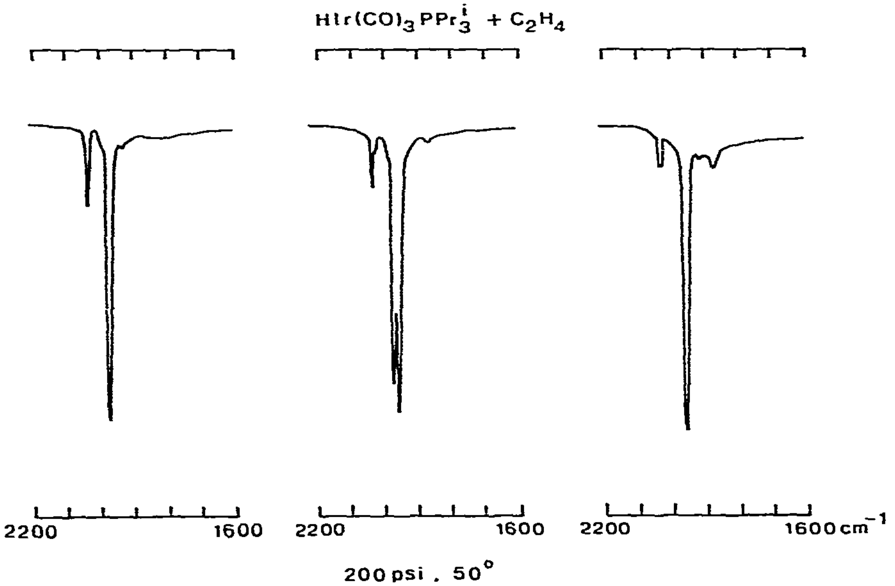


Fig. 2. IR spectral changes during the reaction of $HIr(CO)_3P$-i-Pr_3 and ethylene in heptane.

TABLE 1

IR SPECTRA OF IRIDIUM COMPLEXES OBSERVED IN THE REACTION $HIr(CO)_3P\text{-}i\text{-}Pr_3 + C_2H_4$ IN HEPTANE AND THEIR COBALT ANALOGUES

$C_2H_5Ir(CO)_3P\text{-}i\text{-}Pr_3$	$CH_3Co(CO)_3PBu_3$	$HCo(CO)_3PBu_3$	$HIr(CO)_3P\text{-}i\text{-}Pr_3$
		2050m	2038m
2030w	2034m		
2025w			
		1970s	1970vs
1957s	1955vs		
1954s			
		1933w	1933w
1920vw	1921mw		

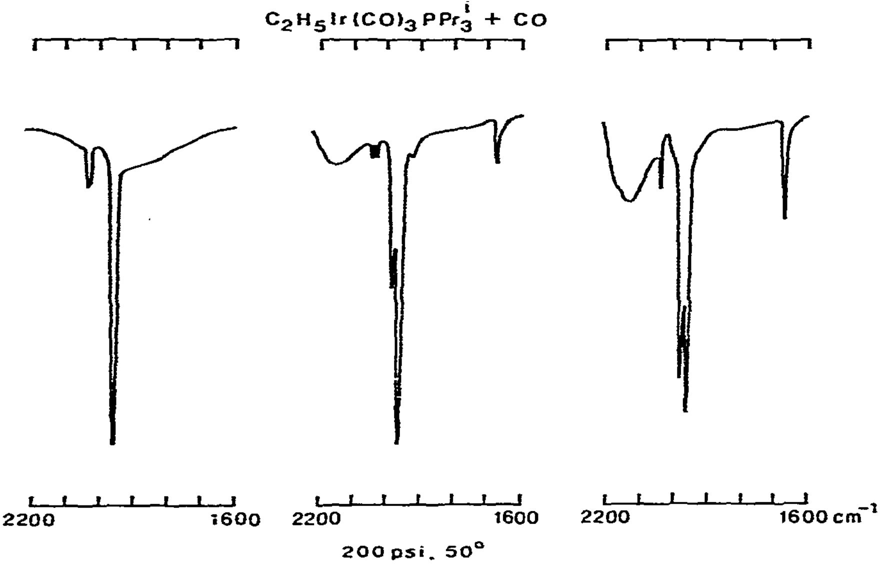


Fig. 3. IR spectral changes during the reaction of $C_2H_5Ir(CO)_3P\text{-}i\text{-}Pr_3$ and carbon monoxide in heptane.

TABLE 2

IR SPECTRA OF IRIDIUM COMPLEXES OBSERVED IN THE REACTION $C_2H_5Ir(CO)_3P\text{-}i\text{-}Pr_3 + CO$ IN HEPTANE, AND A COBALT ANALOGUE

$C_2H_5COIr(CO)_3P\text{-}i\text{-}Pr_3$	$C_2H_5Ir(CO)_3P\text{-}i\text{-}Pr_3$	$C_2H_5COCo(CO)_3PBu_3$
2041w		2042w
	2030w	
	2025w	
1978s		1972s
1959s	1957s	1950s
	1954s	
	1920vw	
1671m		1676m

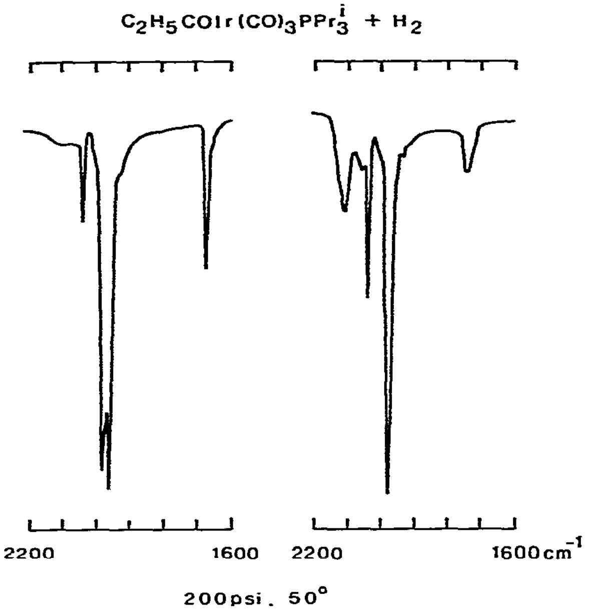


Fig. 4. IR spectral changes during the reaction of $C_2H_5COIr(CO)_3P$-i-Pr_3 and hydrogen.

tained after 30 min is consistent with the conversion of $HIr(CO)_3P$-i-Pr_3 into $C_2H_5Ir(CO)_3P$-i-Pr_3, by comparison with the spectra of related cobalt complexes (Table 1). The methyl complex $CH_3Co(CO)_3PBu_3$ was prepared by Piacenti using a rather different route [5].

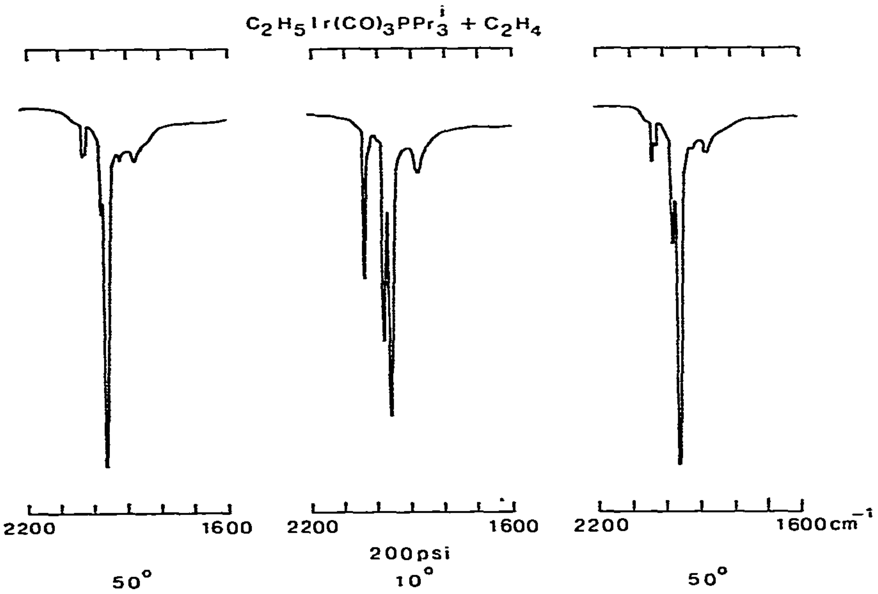


Fig. 5. IR spectral changes observed on cooling the solution from the reaction of $HIr(CO)_3L$ and ethylene in heptane.

On venting the excess ethylene pressure from the solution of the alkyltricarbonyl species and replacing with 200 psi carbon monoxide at 50°C further spectral changes are observed (Fig. 3). Thus, new absorptions appear at 2041, 1978 and 1671 cm^{-1} as the absorption at ca. 1955 cm^{-1} remains approximately constant in intensity. Conversion to the new species is complete after ca. 30 min and again, by comparison with Piacenti's work [5] on the corresponding cobalt complexes (Table 2), the spectral changes correspond with the conversion of $C_2H_5Ir(CO)_3P$-i-Pr_3 into $C_2H_5COIr(CO)_3P$-i-Pr_3 (step 4 in our initial Reaction Scheme 1).

Similarly, on venting the excess carbon monoxide pressure and replacing with 200 psi hydrogen further reaction takes place (Fig. 4) with the disappearance of the bands due to the acyl species, reappearance of the absorptions due to $HIr(CO)_3P$-i-Pr_3 and the appearance of a band at 1730 cm^{-1}. The latter absorption presumably corresponds with the presence of propionaldehyde. Additional absorptions are however noted at 2118, 2105 and 1982 (sh) cm^{-1} and these presumably correspond with the formation of some $H_3Ir(CO)_2P$-i-Pr_3, the triphenylphosphine analogue of which has been described by Malatesta [6]. On replacing hydrogen by carbon monoxide these additional peaks disappear as the intensities of the absorptions due to $HIr(CO)_3P$-i-Pr_3 increase slightly. This behaviour is consistent with the following equilibrium situation:

$$HIr(CO)_3P\text{-i-}Pr_3 + H_2 \rightleftharpoons H_3Ir(CO)_2P\text{-i-}Pr_3 + CO$$

The sequence of reactions described here can be repeated almost indefinitely by pressurising with the respective gases at appropriate times, the intensity of the aldehyde absorption increasing at the end of each cycle. We have thus clearly demonstrated the occurrence of the steps 1, 2 and 3 (combined), 4 and 5 in the proposed hydroformylation sequence; in addition only mononuclear iridium carbonyl species are observed throughout these reactions.

A consideration of the two additional absorptions which were observed after the initial formation of the alkyliridium tricarbonyl species is now appropriate. Spectral changes which are observed on cooling the solution from the reaction of $HIr(CO)_3L$ and ethylene in heptane to room temperature are illustrated in Fig. 5. Two weak absorptions at 2035 and 1974 cm^{-1} increase in intensity as the doublet at ca. 1955 cm^{-1} due to the alkyl tricarbonyl species decreases. On warming to 50°C the original spectrum may be reproduced, leading to the conclusion that we are dealing with a temperature-dependent reversible equilibrium. The intensities of the new absorptions seem to be proportional to the pressure of ethylene; they are not observed when solutions of $C_2H_5Ir(CO)_3L$ are treated with nitrogen, hydrogen or carbon monoxide. With H_2 and CO other reactions are observed, e.g., hydrogenation occurs in the presence of hydrogen with the formation of $HIr(CO)_3P$-i-Pr_3 and presumably, ethane. On pressurising with carbon monoxide at either temperature the two new bands immediately disappear with the reformation of the original alkyl tricarbonyl species, followed by slower conversion into the acyl tricarbonyl, a reaction sequence which may also be reversed on exchanging the CO pressure for ethylene.

The observation of two strong ν(CO) absorptions is consistent with the presence of a dicarbonyl species, although the fact that no reaction occurs under nitrogen appears to rule out a simple coordinative unsaturation effect, i.e.:

$$C_2H_5Ir(CO)_3L \rightleftharpoons C_2H_5Ir(CO)_2L + CO$$

Of the several possibilities available the following explanations for the behaviour seem most likely:

$$C_2H_5Ir(CO)_3L + C_2H_4 \rightleftharpoons C_2H_5Ir(C_2H_4)(CO)_2L + CO$$

or less likely:

$$C_2H_5Ir(CO)_3L \rightleftharpoons H(C_2H_4)Ir(CO)_2L + CO$$

The latter possibility would of course be particularly interesting in view of the identity of the dicarbonyl with the proposed π-complex formed from the initial addition of olefin to $HM(CO)_3L$, i.e. step 2 of our Reaction Scheme 1.

We hope to be able to confirm the nature of the dicarbonyl species by NMR measurements under pressure.

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