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KINETIC STUDY OF THE REACTIONS OF SUBSTITUTED OLEFINS WITH HYDRIDODINITROGENTRIS(TRIPHENYLPHOSPHINE)COBALT(I) AND HYDRIDOCARBONYLTRIS(TRIPHENYLPHOSPHINE)COBALT(I)

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SUMMARY

The reactions of $CoH(N_2)(PPh_3)_3$ (I) and $CoH(CO)(PPh_3)_3$ (II) with substituted olefins have been studied. Some olefins give olefin-coordinated π complexes whereas others are polymerized by (I) and (II). Kinetic studies by a spectroscopic method revealed that the reactions are first-order with respect to the complexes; the pseudo-first-order rate constants $k(N_2)$ and $k(CO)$ of the reactions with the N_2 and CO complexes can be expressed as

$$\frac{1}{k(N_2)} = \frac{1}{k_1} + A\cdot\{B+C\cdot[N_2]\}\cdot\frac{[PPh_3]}{[Olefin]} \tag{1}$$

$$\frac{1}{k(CO)} = \frac{1}{k_1'} + D\,\frac{[PPh_3]}{[Olefin]} \tag{2}$$

On the basis of kinetic results and from the comparison of the reactions of (I) and (II) with olefins, a mechanism involving a dissociation of one triphenylphosphine ligand from (I) and (II), followed by coordination of the olefin leading to the activation of Co–H bonds is proposed.

INTRODUCTION

Complexes having metal–hydrogen and metal–carbon bonds catalyze the homogeneous hydrogenation, oligomerization and polymerization[1]. We have isolated various transition metal complexes containing metal–hydrogen and metal–alkyl bonds from Ziegler type mixed catalyst systems and have studied the reactions of these complexes with various substituted olefins[2]. In some cases the reactions of olefins with the hydride and alkyl complexes lead to polymerization while in other cases metal–olefin π complexes are formed. Previously we reported the isolation of olefin-coordinated complexes by the reactions of methyltris(triphenylphosphine)cobalt(I) and hydridodinitrogentris(triphenylphosphine)cobalt(I) $CoH(N_2)(PPh_3)_3$ with olefins[3]. In this paper we describe the mechanistic studies on the reactions of olefins with $CoH(N_2)(PPh_3)_3$[4] and its isoelectronic analog, hydridocarbonyltris(triphenylphosphine)cobalt(I) $CoH(CO)(PPh_3)_3$[4]. These hydride complexes are stable and proved to be particularly suitable for studying spectroscopically the mechanisms of activation of the metal–hydrogen bond by coordination of olefins.

RESULTS AND DISCUSSION

Reactions of $CoH(N_2)(PPh_3)_3$ with substituted olefins

Table 1 summarizes reactivities and polymerization activities of $CoH(N_2)(PPh_3)_3$ towards a series of vinyl compounds. The olefins are arranged in the decreasing order of Alfrey and Price's *e*-value[5] which is considered to reflect the electronegativity of the olefins. Previously we noted in the reactions of an dialkylbis(bipyridine)iron(II) with olefins that there is a correlation between the *e*-values and the reactivities of the olefins with the alkyliron complex; *i.e.*, the olefins with larger *e*-values, except for α,β-substituted olefins, are polymerized and the olefins with negative *e*-values do not react with the alkyliron complex[2b]. A similar but less marked trend is also observed here in the reactions with (I). Olefins of medium *e*-values are polymerized by (I) but in contrast to the inertness of $R_2Fe(Bipy)_2$ towards olefins with negative *e*-values, (I) reacted with styrene and isobutyl vinyl ether giving olefin-coordinated complexes[3].

In all reactions nitrogen was evolved but hydrogen was not liberated.

TABLE 1

REACTIONS OF $CoH(N_2)(PPh_3)_3$ WITH OLEFINS

Olefin	*e-value*	*Results*[a]
Tetracyanoethylene (TCNE)		$CoH(TCNE)_2(PPh_3)_2$
Acryl amide (Acam)	1.30	$CoH(Acam)_3$
Methacrylamide (Meacam)		$CoH(Meacam)_3$
Acrylonitrile (AN)	1.20	Polymerization
Methacrylonitrile (MAN)	0.81	Polymerization
Acrolein (AC)	0.73	Polymerization
Methyl vinyl ketone (MVK)	0.69	Polymerization
Methyl acrylate (MA)	0.60	Oily product
Methyl methacrylate (MMA)	0.40	Polymerization
Vinyl acetate (Vac)	−0.22	$CoH(Vac)_2$
Styrene (St)	−0.80	$Co(St)(P(C_6H_4)(C_6H_5)_2)(PPh_3)_2$
Isobutyl vinyl ether (IBVE)	−1.77	$CoH(IBVE)_2$

[a] The isolated complexes whose compositions are given in the table have been reported separately[3].

Kinetics of the reactions of $CoH(N_2)(PPh_3)_3$ with olefins

$CoH(N_2)(PPh_3)_3$ exhibits a band of large extinction coefficient ($\varepsilon \approx 3 \times 10^3$) at 390 nm in toluene and a band at 260 nm, at the same wavelength as the absorption of the triphenylphosphine ligand itself. Similar bands are observed with $CoH(CO)(PPh_3)_3$ at 375 and 260 nm in toluene. The absorption of $CoH(N_2)(PPh_3)_3$ at 390 nm may be assigned to a charge-transfer band which is due to an electronic excitation from a cobalt *d*-orbital to an anti-bonding π^* orbital of the triphenylphosphine ligand. The assignment is supported by the blue shifts of the band in polar solvents such as dimethylformamide and acetonitrile. In these solvents the energy of the *d*-orbitals are considered to be lowered by strong solvent-coordination*. That $CoH(CO)(PPh_3)_3$ shows a similar band at 375 nm in toluene also supports the assignment, since the CO ligand, being a stronger π acceptor than N_2, may cause the lowering of the *d*-orbitals thus leading to the blue shift from the absorption band of $CoH(N_2)(PPh_3)_3$.

The reactions of $CoH(N_2)(PPh_3)_3$ with olefins can be conveniently followed by observing the spectral change in the charge-transfer band as exemplified in Fig. 1 (reaction of $CoH(N_2)(PPh_3)_3$ with styrene). The charge-transfer band at 390 nm decreases with time, the spectrum showing clear isosbestic points. In Fig. 2, plots of the logarithms of the absorbances $(A - A_\infty)$, where A_∞ represents the absorbance at the

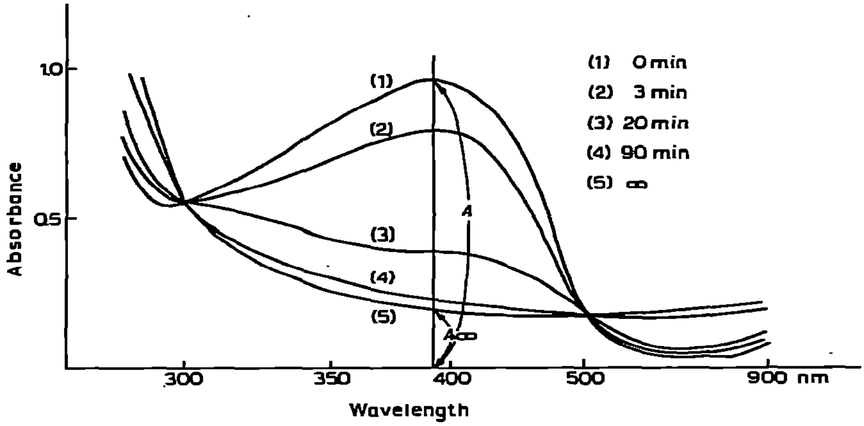

Fig. 1. The spectral change of $CoH(N_2)(PPh_3)_3$ upon reaction with styrene in toluene at 25°; $[CoH(N_2)(PPh_3)_3] = 4.4 \times 10^{-4}$ mol/l, $[\text{Styrene}] = 2.2 \times 10^{-2}$ mol/l, (1) 0 min, (2) 3 min, (3) 20 min, (4) 90 min, (5) ∞.

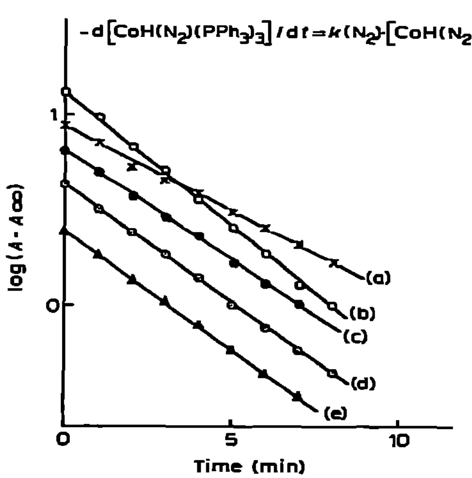

Fig. 2. Plots of log $(A - A\infty)$ (*cf.* Fig. 1) *vs.* time; (a) methacrylonitrile (MAN), 1.80×10^{-2} mol/l; (b) methyl acrylate (MA), 3.62×10^{-2} mol/l; (c) acrylonitrile (AN), 2.20×10^{-2} mol/l; (d) methylmethacrylate (MMA), 2.00×10^{-2} mol/l; (e) styrene (St), 1.25×10^{-2} mol/l; at 25°, in toluene.

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* In fact an acetonitrile coordinate complex has been isolated[6].

end of the reaction in Fig. 1, against time indicate that the reaction is first-order with respect to $CoH(N_2)(PPh_3)_3$ under the conditions where the changes of olefin concentration are negligible.

$$-d[CoH(N_2)(PPh_3)_3]/dt = k(N_2) \cdot [CoH(N_2)(PPh_3)_3] \qquad (1)$$

Eqn. (1) holds for the reactions with acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate and styrene. When the olefin concentrations are varied, $k(N_2)$ in eqn. (1) increases with increasing olefin concentration approaching a limiting value, designated as k_1 in Fig. 3. Fig. 4 shows the linear relationship between $1/k(N_2)$ and $1/[M]$ (where $[M]$ is the olefin concentration) which were replotted from Fig. 3. The kinetic results suggest an S_N1 mechanism for the reactions of $CoH(N_2)(PPh_3)_3$ with olefins where a slow ligand dissociation takes place first followed by interaction of the olefin with the partially dissociated complex leading to the irreversible change

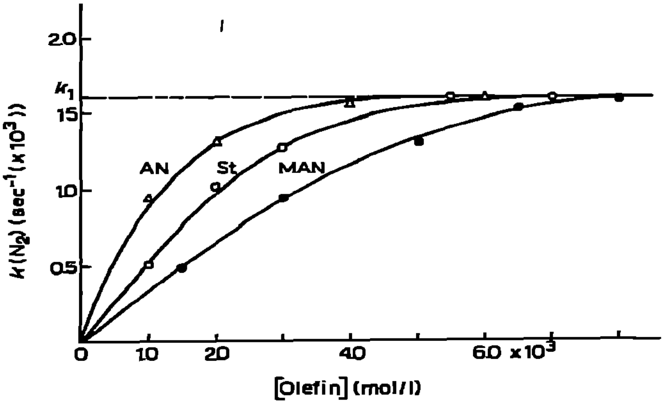

Fig. 3. Pseudo-first-order rate constant $k(N_2)$ vs. olefins concentration at 25°; solvent = toluene, AN = acrylonitrile, St = styrene, and MAN = methacrylonitrile, $[CoH(N_2)(PPh_3)_3] = 3.6 \times 10^{-4}$ mol/L.

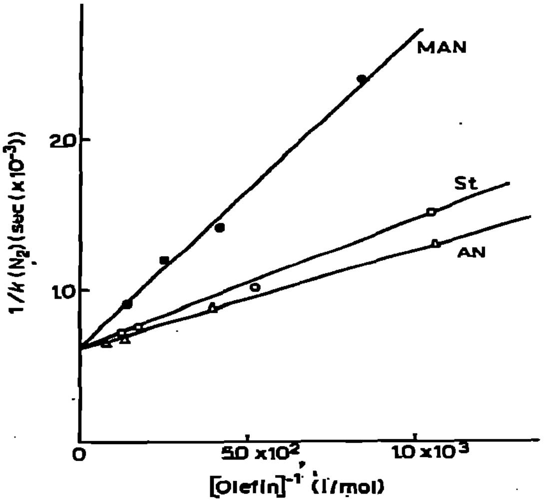

Fig. 4. The reciprocal plot for the data shown in Fig. 3.

of the complex. Either dinitrogen or triphenylphosphine should be considered as the leaving ligand and this presents a difficult problem, namely to decide which is the actual leaving group. Although the formations of $CoH(CO)(PPh_3)_3$ and Co(Styrene)-$(P(C_6H_4)Ph_2)(PPh_3)_2$[3] in the reactions of $CoH(N_2)(PPh_3)_3$ with CO and styrene appear to support initial liberation of N_2, the kinetic results based on inhibition experiments in the presence of added triphenylphosphine in the reactions of $CoH(N_2)$-$(PPh_3)_3$ with olefins is compatible with a mechanism involving initial liberation of triphenylphosphine. Fig. 5 demonstrates the effect of addition of triphenylphosphine

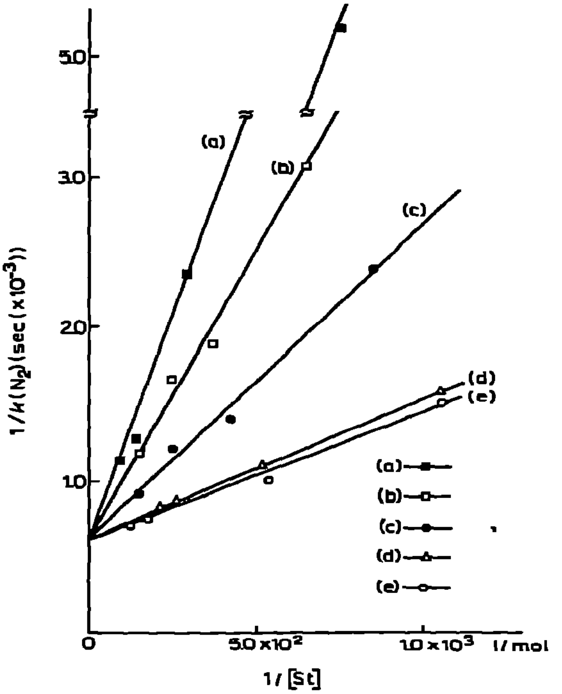

Fig. 5. The effect of added triphenylphosphine on the pseudo-first-order rate constant, $k(N_2)$, for the reaction of $CoH(N_2)(PPh_3)_3$ with styrene in toluene at 25°; added $[PPh_3]$: (a) 4.27×10^{-3}; (b) 1.95×10^{-3}; (c) 1.45×10^{-3}; (d) 0.55×10^{-3}; (e) 0 mol/l.

on the rate constants $k(N_2)$ in the reaction of $CoH(N_2)(PPh_3)_3$ with styrene. The reaction is suppressed in the presence of added triphenylphosphine and the rate dependence on the concentration of added triphenylphosphine is shown in Fig. 6. The effect of nitrogen pressure on the reaction rates was also studied by varying the pressure of nitrogen gas in the presence of added triphenylphosphine and at constant concentration of methacrylonitrile. Fig. 7 illustrates the result showing a linear relationship between $1/(k(N_2)$ and $P(N_2)$, the pressure of nitrogen, except for the low $P(N_2)$ region where some deviation from the linearity is observed.

These results can be interpreted in terms of a mechanism comprising the following elementary steps:

$$\underset{[C_1]}{\mathrm{CoH(N_2)(PPh_3)_3}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{[C_2]}{\mathrm{CoH(N_2)(PPh_3)_2}} + \mathrm{PPh_3} \qquad \text{(a)}$$

$$\underset{[C_2]}{\mathrm{CoH(N_2)(PPh_3)_2}} + \mathrm{Olefin} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{[C_3]}{\mathrm{CoH(N_2)(Olefin)(PPh_3)_2}} \qquad \text{(b)}$$

$$\underset{[C_3]}{\mathrm{CoH(N_2)(Olefin)(PPh_3)_2}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{[C_4]}{\mathrm{CoH(Olefin)(PPh_3)_2}} + \mathrm{N_2} \qquad \text{(c)}$$

$$\underset{[C_4]}{\mathrm{CoH(Olefin)(PPh_3)_2}} \xrightarrow{k_4} \text{irreversible reaction} \qquad \text{(d)}$$

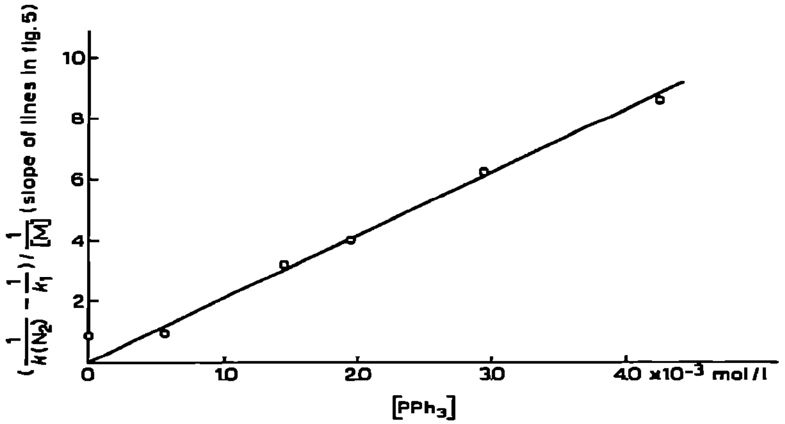

Fig. 6. The plot of the slopes of lines in Fig. 5 against the concentration of added triphenylphosphine.

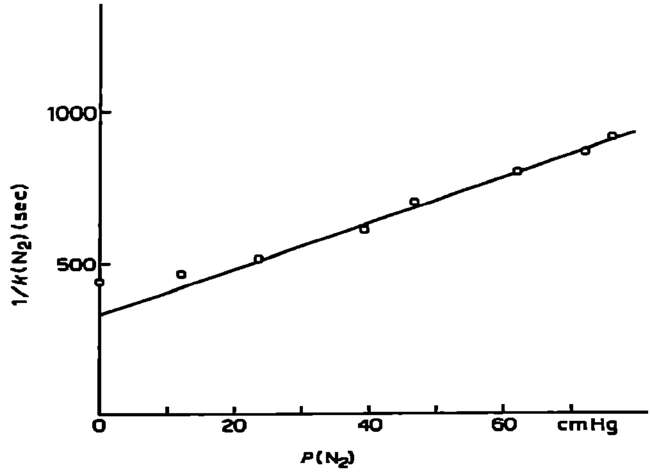

Fig. 7. The effect of the pressure of nitrogen on the pseudo-first-order rate constant $k(N_2)$ for the reaction of $\mathrm{CoH(N_2)(PPh_3)_3}$ with methacrylonitrile in tetrahydrofuran at 35°. [methacrylonitrile] $= 7.5 \times 10^{-2}$ mol/l; $[\mathrm{PPh_3}] = 8.55 \times 10^{-3}$ mol/l; $[\mathrm{CoH(N_2)(PPh_3)_3}] = 5.70 \times 10^{-4}$ mol/l.

In step (a) triphenylphosphine is removed, making a site available for the incoming olefin which coordinates to the partially dissociated species $[C_2]$ in step (b). By interaction of the olefin with cobalt a π complex $[C_3]$ is formed in which the electron density on cobalt is decreased because of back-donation from cobalt to the olefin. The decrease in electron density in $[C_3]$ makes the back-donation from cobalt to the N_2 ligand less favorable thus leading to the dissociation of N_2 in step (c). In step (d) the coordinated olefin activates the Co–H bond and consequently an irreversible reaction, such as polymerization and the formation of the complexes given in Table 1, takes place. Step (d) is rate-determining at low olefin concentrations whereas at high olefin concentrations, the rate is determined by step (a). In the reaction of styrene with (I) ethylbenzene and a styrene-coordinated complex $Co(Styrene)[P(C_6H_4)Ph_2](PPh_3)_2$ are formed[3]. As illustrated by the formation of $Co(Styrene)[P(C_6H_4)Ph_2](PPh_3)_2$, the mechanism may be further complicated by involvement of the *ortho*-hydrogens of the triphenylphosphine ligand, but in order to avoid undue complications we confine ourselves to the discussion of the reaction mechanism expressed by steps (a) to (d) which are relevant to the understanding of the essential mechanism. The assumption of steps (a) to (d) and the stationary state approximation for the concentrations of $[C_2]$, $[C_3]$ and $[C_4]$ leads to eqns. (1) and (2).

$$\frac{1}{k(N_2)} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 \cdot k_2 \cdot k_3} \cdot \frac{[PPh_3]}{[M]} \cdot \{(k_{-2}+k_{-3}) + \frac{k_{-2} \cdot k_{-3}}{k_4} \cdot [N_2]\} \qquad (2)$$

The essential agreement of eqn. (2) with the experimental results shown in Figs. 4–7 is evident. A mechanism assuming initial removal of N_2 cannot account for the inhibiting effect of triphenylphosphine. The following independent lines of evidence also support initial liberation of triphenylphosphine. (*i*). The N_2 ligand in $CoH(N_2)(PPh_3)_3$ is firmly bound to cobalt and it is difficult to remove N_2 from the solid complex by pumping; slow evolution of N_2 starts at ca. 80° accompanied by irreversible decomposition of the complex[4]. (*ii*). The exchange of coordinated $^{28}N_2$ in $CoH(N_2)(PPh_3)_3$ dissolved in benzene with gaseous $^{30}N_2$ failed[4]. (*iii*). An infrared study revealed that the replacement of the coordinated triphenylphosphine in the N_2 complex by free tributylphosphine or trioctylphosphine in benzene solution took place in a stepwise manner to the extent that the three triphenylphosphine ligands were displaced by trialkylphosphine molecules without decrease in the intensity of the $\nu(N{\equiv}N)$ absorption[4]. The isolation of complexes containing three coordinated triphenylphosphine ligands such as $CoH(CO)(PPh_3)_3$, and $Co(Styrene)[P(C_6H_4)Ph_2](PPh_3)_2$ after reaction of $CoH(N_2)(PPh_3)_3$ with CO and styrene may at first sight appear incompatible with the present mechanism assuming liberation of triphenylphosphine, but examples are known where the liberated ligand combines with the complex to give a less soluble and isolable complex and the isolation of a complex with three triphenylphosphine ligands does not preclude the liberation of the ligand in solution.

In order to obtain evidence for the slow liberation of triphenylphosphine in solution the variable temperature ^{31}P NMR spectra of (I) in toluene were measured. The proton decoupled ^{31}P NMR spectrum of (I) at room temperature showed a somewhat broad single peak due to coordinated triphenylphosphine ligands at −49.4 ppm (relative to the peak for free triphenylphosphine as the external standard); no peak due to liberated triphenylphosphine was observed. A toluene solution of (I) containing added triphenylphosphine in a 1/1 ratio showed single peaks due to coordinated and to free triphenylphosphine in a 3/1 ratio. By lowering the temperature to −80° a striking sharpening of the peaks of both the coordinated and the free triphenylphosphine and an increase of the chemical shift difference between the two peaks to 52.9 ppm took place. These results indicate that in the concentration range, suitable for the observation of the ^{31}P NMR (ca. 10%), the equilibrium [eqn. (a)] lies to the left and that the concentration of free triphenylphosphine is negligible, but that slow exchange does take place at room temperature. In the context of the proposed mechanism, the k_1 value corresponding to the rate constant for the liberation of triphenylphosphine from (I) in eqn. (a) is 1.6×10^{-3} sec^{-1} from Fig. 3. This value is quite small in the time scale of ^{31}P NMR at 40 MHz and it is reasonable that the somewhat broadened peaks of the coordinated and uncoordinated triphenylphosphines as separate peaks at room temperature should be observed.

Some experimental deviation from the relationship expressed by eqn. (2) demands comment. Although eqn. (2) requires that the line in Fig. 6 should pass through the origin, the ordinate of Fig. 6, in the absence of added triphenylphosphine, has a definite positive value. This is probably caused by the liberation of triphenylphosphine from (I) in the solution, when the concentration of (I) is too low to allow the measurement of the electronic spectrum, and the actual concentration of the triphenylphosphine in the solution is not zero. Fig. 7 also exhibits deviation from linearity in the low $P(N_2)$ range expected from eqn. (2). Although the exact reason for the deviation is not apparent from the available data, it is possible that initial liberation of the N_2 ligand is taking place to a minor extent compared with the major first removal of the triphenylphosphine ligand, particularly in the low $P(N_2)$ region. If this is the case, the actual $P(N_2)$ values at low nitrogen pressures in Fig. 7 should be increased, a better agreement of the experimental values with the linearity being thus obtained. In general, the proposed mechanistic scheme (a) to (d) is in agreement with the experimental results.

Kinetics of the reactions of $CoH(CO)(PPh_3)_3$ with olefins

$CoH(CO)(PPh_3)_3$ reacts with various substituted olefins to give polymers or

TABLE 2

REACTIONS OF $CoH(CO)(PPh_3)_3$ WITH OLEFINS[a]

Olefin	*e-value*	*Results*
Tetracyanoethylene (TCNE)		$CoH(CO)(TCNE)_2(PPh_3)_2$
Acrylamide (Acam)	1.30	$CoH(CO)(Acam)_3$
Acrylonitrile (AN)	1.20	Polymerization
Methacrylonitrile (MAN)	0.81	Reaction[b]
Methyl acrylate (MA)	0.60	No reaction
Methyl methacrylate (MMA)	0.40	No reaction
Vinyl acetate (Vac)	−0.22	$CoH(CO)(Vac)_2$
Styrene (St)	−0.80	Polymerization
α-Methyl styrene (α-Mest)		No reaction
Isobutyl vinyl ether (IBVE)	−1.77	Polymerization[c]
Butadiene (BD)		No reaction

[a] All the reactions were carried out at room temperature. [b] The color of the complex changed to green without evolving gas. [c] A polymer of low molecular weight soluble in methanol was obtained.

olefin-coordinated complexes (see Experimental). Table 2 summarizes the reactivities and polymerization activities of $CoH(CO)(PPh_3)_3$ towards olefins. Evidently the carbonyl complex is less active than its isoelectronic analog $CoH(N_2)(PPh_3)_3$ and only a limited number of vinyl compounds were polymerized. In the reactions of $CoH(CO)(PPh_3)_3$ with tetracyanoethylene, vinyl acetate, and acrylamide, carbon monoxide and hydrogen were not evolved and the carbonyl ligand remained attached to cobalt throughout.

Quite analogously to the corresponding dinitrogen complex, the reactions of $CoH(CO)(PPh_3)_3$ with olefins were followed by observing the spectral change of its charge-transfer band at 375 nm. The reaction was first-order with respect to $CoH(CO)(PPh_3)_3$ and the concentration change in the olefin can be ignored.

$$-d[CoH(CO)(PPh_3)_3]/dt = k(CO)\cdot[CoH(CO)(PPh_3)_3] \qquad (3)$$

The pseudo-first-order rate constant $k(CO)$ increased with increasing olefin concentration, approaching a limiting value k_1'. The reciprocal plots of $k(CO)$ against methacrylonitrile concentration are linear as shown in Fig. 8. Addition of triphenylphosphine to the system inhibited the reaction. A similar plot to Fig. 6 gave Fig. 9. The interpretation of the kinetic results for the present system is more straightforward than that with the dinitrogen complex. The carbonyl ligand is more strongly bound to cobalt than is dinitrogen in $CoH(N_2)(PPh_3)_3$ and triphenylphosphine can be

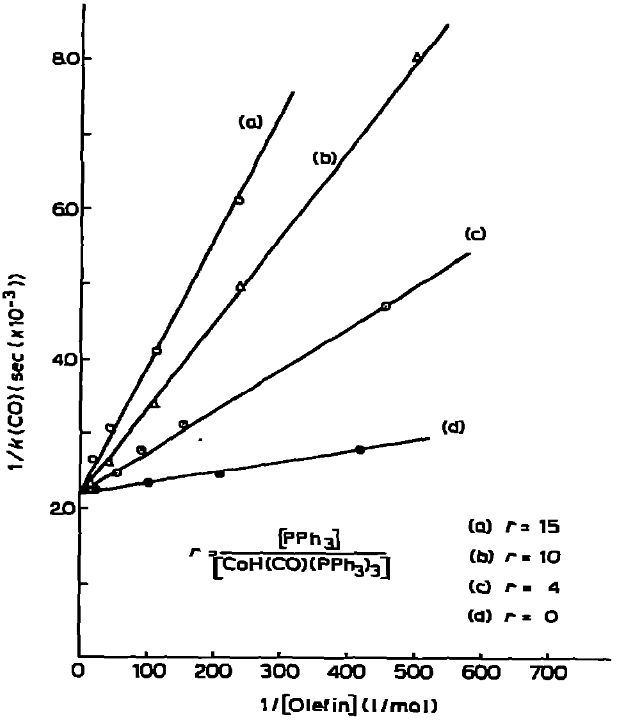

Fig. 8. The effect of added triphenylphosphine on the pseudo-first-order rate constant, $k(CO)$ for the reaction of $CoH(CO)(PPh_3)_3$ with methacrylonitrile in toluene at 35°. $[PPh_3]$: (a) 2.56×10^{-3}; (b) 1.70×10^{-3}; (c) 0.62×10^{-3}; (d) 0 mol/l.

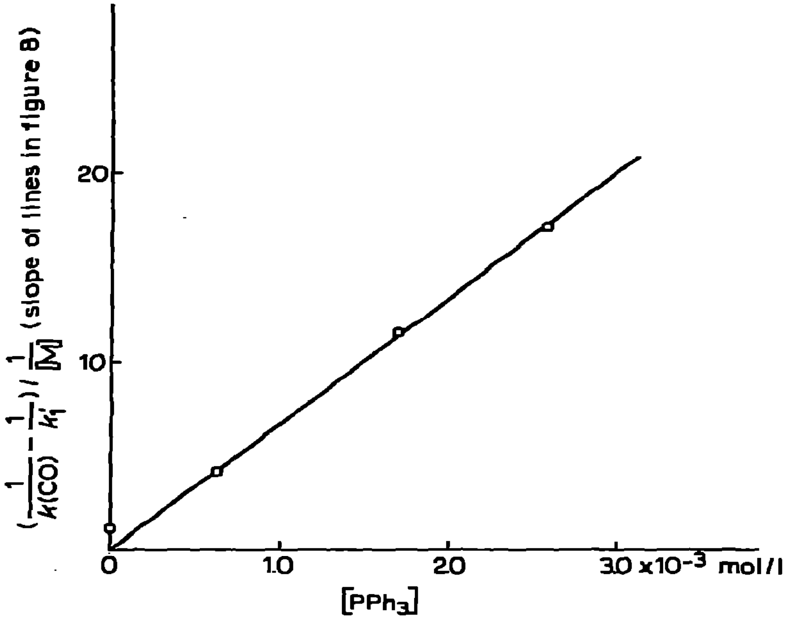

Fig. 9. The plot of the slopes of lines in Fig. 8 against the added triphenylphosphine, $[PPh_3]$.

safely regarded as the dominant first liberated ligand. The kinetic results can be explained by assuming the following elementary processes: (a)' liberation of triphenylphosphine from the carbonyl complex making a coordination site free; (b)' coordination of the olefin to the vacant site; (c)' by coordination of the olefin, the Co–H bond is activated and the complex decomposed irreversibly or a polymer is formed by insertion of the olefin into the Co–H bond.

$$\underset{[C'_1]}{CoH(CO)(PPh_3)_3} \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} \underset{[C'_2]}{CoH(CO)(PPh_3)_2} + PPh_3 \qquad (a)'$$

$$\underset{[C'_2]}{CoH(CO)(PPh_3)_2} + \text{olefin} \underset{k'_{-2}}{\overset{k'_2}{\rightleftharpoons}} \underset{[C'_3]}{CoH(CO)(\text{olefin})(PPh_3)_2} \qquad (b)'$$

$$\underset{[C'_3]}{CoH(CO)(\text{olefin})(PPh_3)_2} \xrightarrow{k'_3} \text{irreversible reaction} \qquad (c)'$$

The assumption of these elementary steps with (c)' as the rate-determining step, when a limited amount of olefin was used, and the application of the steady-state approximation to the concentrations $[C'_2]$ and $[C'_3]$ leads to eqns. (3) and (4) which are in agreement with the experimental results shown in Figs. 8 and 9.

$$\frac{1}{k(CO)} = \frac{1}{k'_1} + \frac{k'_{-1}\cdot k'_{-2}}{k'_1\cdot k'_2\cdot k'_3}\cdot\frac{[PPh_3]}{[M]} \qquad (4)$$

If the proposed mechanism is valid, k'_1, the rate constant for the initial liberation of triphenylphosphine from the carbonyl complex is smaller than k_1, the rate constant for triphenylphosphine liberation from the dinitrogen complex. This is reasonable because the carbonyl ligand, being a better π-acceptor than dinitrogen, will make the liberation of triphenylphosphine more difficult if it is acting mainly as a σ Lewis base.

Fig. 9 also shows the similar trend of the deviation from linearity to the case with (I) in the absence of added triphenylphosphine, and a similar discussion may be applied here. The smaller deviation from the linearity in Fig. 9 as compared with Fig. 6 may be taken as the indirect evidence to show that the triphenylphosphine ligand is dissociated to a smaller extent from (II) than from (I) in the low concentration range of the added triphenylphosphine.

The difference in the catalytic activities between the dinitrogen and the carbonyl complexes may be related with the difference in the Lewis basicities or to the difference in the energy levels of the *d*-orbitals of the two complexes. If back-donation from cobalt to the olefin is the dominant factor in determining the strength of the interaction between cobalt and the olefin, the stronger interaction is expected between the more basic complex and the electronegative olefin, *i.e.* between the cobalt complex with higher *d*-orbitals and the olefin, and the stronger interaction between the cobalt and the olefin is anticipated to lead to the more enhanced activation of the olefin. This accounts for the fact that only a limited number of electronegative olefins can be polymerized by the carbonyl complex which can be regarded as less basic than the dinitrogen complex. That the carbonyl complex shows the charge-transfer band at shorter wavelength than the dinitrogen complex suggests the lower *d*-orbitals of the carbonyl complex as previously discussed.

In conclusion, the essential features of the kinetics resemble those of the reactions of dialkylbis(dipyridyl)iron(II) complex with olefins[2b] and also those of dihydridotetrakis(triphenylphosphine)ruthenium(II)[7]. The common features of the reactions of these reactions may be summarized as follows: (*i*) partial dissociation of the ligands from the complex; (*ii*). coordination of the olefin to the vacant site which thus becomes available; (*iii*). activation of the coordinated olefin and of the metal–carbon or metal–hydrogen bond, (*iv*). fission of the metal–carbon or metal–hydrogen bond accompanied in some cases by insertion of the olefin. The present results demonstrate clearly how the nature of the ligands can modify the activity and the catalytic reactivities of the transition metal complexes.

EXPERIMENTAL SECTION

I. Materials

$CoH(N_2)(PPh_3)_3$ and $CoH(CO)(PPh_3)_3$ were prepared using the methods described in our previous paper[4]. Solvents and liquid olefins were dehydrated, distilled and stored under nitrogen before use.

II. Reactions of $CoH(CO)(PPh_3)_3$ with olefins and isolations of olefin-coordinated cobalt complexes

Reactions of $CoH(N_2)(PPh_3)_3$ have been reported separately[3] and the reactions of $CoH(CO)(PPh_3)_3$ with olefins are here described.

(1). *Tetracyanoethylene (TCNE)*. A mixture of 110 mg (0.13 mmol) of $CoH(CO)(PPh_3)_3$ and 150 mg of TCNE (1.28 mmol) in 10 ml of toluene was allowed to react for 1 day.

at room temperature. No evolution of gas was observed. The light brown complex formed was filtered and washed several times with hexane, and dried under vacuum. Yield 30%. IR (KBr): $\nu(C\equiv N)$, 2220 and 2150 cm^{-1}; $\nu(Co{-}H)$, 2000 cm^{-1}; $\nu(C\equiv O)$, 1950 cm^{-1}. (Found: C, 68.2; H, 4.2; N, 11.7; $C_{49}H_{31}CoN_8OP_2$ calcd.: C, 67.7; H, 3.6; N, 12.9%.)

(2). *Acrylamide* (*Acam*). A mixture of 200 mg (0.23 mmol) of $CoH(CO)(PPh_3)_3$ and 60 mg (0.85 mmol) of acrylamide in 15 ml of toluene was stirred for 2 days at room temperature. No gas was evolved. The blue precipitate obtained was filtered and washed repeatedly with hexane, and dried under vacuum. From the filtrate and washings 0.64 mmol of triphenylphosphine was recovered. The yield of the blue complex as $CoH(CO)(Acam)_3$ was 40%. IR(KBr): $\nu(N{-}H)$, 3310 and 3200 cm^{-1}; $\nu(Co{-}H)$, 1970 cm^{-1}; $\nu(C\equiv O)$, 1950 cm^{-1}; $\nu(C{=}C)$, 1645 cm^{-1}; $\nu(C{=}O)$ of amide, 1560–70 cm^{-1}. (Found: C, 51.5; H, 6.3; N, 14.1. $C_{10}H_{16}CoN_3O_4$ calcd.: C, 52.2; H, 7.0; N, 14.0%.)

(3). *Vinyl acetate* (*Vac*). Vinyl acetate (5.0 ml, 47 mmol) was introduced to 120 mg (0.14 mmol) of $CoH(CO)(PPh_3)_3$ with a trap-to-trap distillation. The mixture was stirred for 6 days at room temperature and a light pink complex was precipitated. No gas was evolved and PPh_3 was released quantitatively. The light pink complex was filtered and washed repeatedly with hexane, and dried under vacuum. The yield of the light pink complex as $CoH(CO)(Vac)_2$ is 70%. IR (KBr): $\nu(Co{-}H)$ 1950 cm^{-1}; $\nu(C\equiv O)$ 1740 cm^{-1}; $\nu(C{=}O)$ of acetate 1550–70 cm^{-1}. (Found: C, 40.0; H, 4.3. $C_9H_{13}CoO_5$ calcd.: C, 41.2; H, 5.0%.)

(4). *Polymerization of acrylonitrile, styrene and isobutyl vinyl ether.* These olefins were polymerized with $CoH(CO)(PPh_3)_3$ at room temperature. No gas was evolved in the polymerization.

III. Spectral measurements

The infrared spectra were recorded with a Hitachi Model EPI-G3. The visible and ultraviolet spectra were measured by a Shimazu type SV-50A spectrometer. The complexes and solvents were transferred to the cell under nitrogen and olefins were added by using a syringe. When necessary, the temperature was controlled within 0.5° by circulating water of a constant temperature around the cell. ^{31}P NMR spectra of $CoH(N_2)(PPh_3)_3$ and PPh_3 in toluene (ca. 10 w/v%) were obtained with a JEOL PS-100 spectrometer at 40 MHz using a hetero spin-decoupling technique. The spectrum at room temperature was time-averaged by employment of JEOL EC-5 computer but this procedure was uncessary for the low temperature spectra for the sharpness of the signals.

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