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CHEMISTRY OF THE TRICOBALT—CARBON CLUSTER

XII*. KINETICS OF PHOSPHINE SUBSTITUTION REACTIONS

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Summary

A study is described of the influence of the apical group Y on the kinetics of substitution reactions of $YCCo_3(CO)_9$ (Y = Ph, Me, H, Cl, F) with Ph_3P, Ph_3As and n-Bu_3As. A dissociative mechanism is observed in all cases.

Introduction

Factors which determine the often unusual reactivity of tricobalt—carbon clusters towards Lewis bases [2], unsaturated organic species [1,3], and a variety of nucleophiles [4,5] and electrophiles [4-8] have been elucidated in the last few years. It is clear that the Co_3C core is a delocalised system ("electron reservoir") which withdraws or donates electrons as the situation demands, and that the groups on the cobalt atoms or apical carbon are in a congested environment [9]. Nevertheless, these conclusions come from chemical and structural studies [9] and there is little complimentary kinetic, thermodynamic or theoretical data. This paper describes a kinetic investigation of the reactions between phosphines and enneacarbonylmethinyltricobalt clusters, $YCCo_3(CO)_9$ (Y = Ph, Me, H, Cl, F).

Cetini and coworkers have studied the rate of ^{14}CO exchange and noted that the rate fell in the order Y = F > H > Me ~ Ph [10]. Moreover, three (presumably axial) carbonyl groups underwent faster exchange than the other six except when Y = COOH when only one CO exchanged at a different rate. This could be the >CO of the apical carboxyl group; mass spectral studies show that this CO group is particularly labile [5,11].

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[*] For part XI see ref. 1.

Experimental

The clusters, $YCCo_3(CO)_9$, were prepared and purified according to published procedures [9,12] and all solvents were dried and kept over molecular sieves. Triphenylphosphine and triphenylarsine were commercial reagents (B.D.H.) while n-tributylarsine was prepared from arsenic trichloride and n-butyl lithium.

Kinetic measurements

The reactions were carried out in a nitrogen atmosphere in a three-necked flask (50 cm^3) fitted with a reflux condenser, nitrogen inlet, stirrer and a syringe cap. This flask was suspended in a thermostatted water bath ($\pm 0.1°$) and solutions of the reagents, equilibrated to bath temperature, added at time zero. Aliquots (1 cm^3) of the reaction solution were subsequently withdrawn, by syringe, at approximately five minute intervals and the IR spectrum recorded on a Perkin — Elmer 225 or Jasco IRA-2 spectrophotometer using 0.5 mm NaCl cells.

Reactions were monitored using the symmetrical in-phase stretching mode of the products ($\nu(CO) \approx 2076$ cm^{-1}). This band is particularly suitable because of its relative isolation from other bands and the higher extinction coefficient compared to that of the A_1 mode of the parent cluster. The Beer-Lambert law was found to hold in hexane for the A_1 mode of $PhCCo_3(CO)_8PPh_3$ over a wide range of concentrations and on the basis of earlier work [2], the extinction coefficient ($\epsilon = 532$ $m^2 mol^{-1}$) was assumed to be the same for other $YCCo_3(CO)_8$-PPh_3 derivatives in hexane.

Comparison of the IR spectrum of a run, after several half-lives, with that of the pure product [2] confirmed that all kinetic runs went to completion to the one product in hexane. Good linear plots of $\log_{10}(A-A_\infty)$ versus time were obtained. However, unsatisfactory plots were obtained using chlorinated solvents because of product decomposition during the reaction. This was reflected in lower k_{obs} values (Table 1). In most cases the runs were carried out under pseudo first-order conditions with at least a 10-fold excess of ligand.

TABLE 1

TYPICAL RATE CONSTANTS FOR PHOSPHINE SUBSTITUTION REACTIONS OF $YCCo_3(CO)_9$ [a]

$[YCCo_3(CO)_9]$ (10^{-3} mol dm^{-3})	Ligand	[Ligand] (10^{-3} mol dm^{-3})	T (K)	k_{obs} (10^{-5} sec^{-1})
$Y = Me$				
1.68	Ph_3P	1.64	314.2	2.2
1.66	Ph_3P	1.10	314.2	2.3
1.68	Ph_3P	0.60	314.2	2.2
1.89	Ph_3P	3.09	318.8	3.2
1.61	Ph_3P	2.11	318.8	3.9
2.03	Ph_3P	3.39	323.2	6.9
1.90	Ph_3P	2.68	323.2	6.3 [b]
1.57	Ph_3P	1.75	323.2	6.5
1.56	Ph_3P	0.78	323.2	6.5
0.79	Ph_3P	1.83	323.2	6.5

(continued)

TABLE 1 (continued)

$[\mathrm{YCCo_3(CO)_9}]$ (10^{-3} mol dm^{-3})	Ligand	[Ligand] (10^{-3} mol dm^{-3})	T (K)	k_{obs} (10^{-5} sec^{-1})
3.60	$\mathrm{Ph_3P}$	2.12	323.2	6.9
1.74	$\mathrm{Ph_3P}$	2.47	323.5	6.8
1.75	$\mathrm{Ph_3P}$	2.29	328.4	13.0
1.70	$\mathrm{Ph_3P}$	2.26	332.7	19.4
1.57	$\mathrm{Ph_3P}$	2.50	333.3	22.0
1.86	$\mathrm{Ph_3P}$	2.50	337.5	32.2
Y = H				
2.10	$\mathrm{Ph_3P}$	2.93	313.8	1.0
3.03	$\mathrm{Ph_3P}$	5.47	320.2	3.3
3.35	$\mathrm{Ph_3P}$	4.20	323.6	5.7
2.95	$\mathrm{Ph_3P}$	5.07	325.3	5.1
2.38	$\mathrm{Ph_3P}$	4.28	325.9	7.0
2.27	$\mathrm{Ph_3P}$	4.58	328.4	6.6
2.39	$\mathrm{Ph_3P}$	4.84	329.9	8.5
2.04	$\mathrm{Ph_3P}$	4.21	330.0	9.4
Y = F				
1.64	$\mathrm{Ph_3P}$	2.36	308.4	5.2
1.78	$\mathrm{Ph_3P}$	2.43	309.4	5.5
1.66	$\mathrm{Ph_3P}$	2.13	313.7	8.3
1.66	$\mathrm{Ph_3P}$	2.13	314.5	11.0
1.58	$\mathrm{Ph_3As}$	2.34	314.5	9.0
1.73	$\mathrm{Ph_3P}$	2.52	315.2	9.5
1.53	$\mathrm{Ph_3P}$	2.29	318.8	11.6
1.53	$\mathrm{Ph_3P}$	2.29	319.3	15.0
1.52	$\mathrm{Ph_3As}$	2.29	319.3	19.0
1.39	$\mathrm{Ph_3P}$	2.31	323.7	23.8
1.53	$\mathrm{Ph_3P}$	2.27	324.2	30.2
1.41	$\mathrm{Ph_3P}$	2.22	328.4	48.4
Y = Ph				
2.10	$\mathrm{Ph_3P}$	4.23	308.3	3.6
1.33	$\mathrm{Ph_3P}$	2.19	314.0	7.2
1.60	$\mathrm{Ph_3P}$	3.11	314.7	4.5^c
1.40	$\mathrm{Ph_3P}$	3.08	314.8	9.8
1.42	$\mathrm{Ph_3P}$	2.78	318.2	6.3^c
1.44	$\mathrm{Ph_3P}$	2.27	319.0	16.0
1.42	$\mathrm{Ph_3P}$	2.85	319.3	14.6
1.40	$\mathrm{Ph_3P}$	2.34	323.2	22.0
1.40	$\mathrm{Ph_3P}$	2.45	323.2	15.0^c
0.96	$\mathrm{Ph_3P}$	1.75	323.2	26.0
1.26	$\mathrm{Ph_3P}$	4.90	323.2	23.0
2.02	$\mathrm{Ph_3P}$	4.31	323.2	23.0
3.08	$\mathrm{Ph_3P}$	1.75	323.2	23.0
1.06	$n\text{-}\mathrm{Bu_3As}$	2.03	323.2	19.0
1.33	$n\text{-}\mathrm{Bu_3As}$	2.03	323.2	21.0^d
0.90	$n\text{-}\mathrm{Bu_3As}$	0.97	323.2	27.0
1.75	$n\text{-}\mathrm{Bu_3As}$	0.85	323.2	29.0
1.33	$n\text{-}\mathrm{Bu_3As}$	2.03	323.2	24.0
1.40	$\mathrm{Ph_3P}$	2.34	325.0	34.5
1.37	$\mathrm{Ph_3P}$	2.27	327.7	27.6^c
1.41	$\mathrm{Ph_3P}$	2.19	330.4	33.6

[a] In hexane, unless stated otherwise. [b] Under CO atmosphere. [c] In chloroform. [d] In toluene.

Enthalpies and entropies of activation were determined by a least squares analysis of Arrhenius plots; errors in E_a are estimated as ±4 KJ mol^{-1} and ±8 J mol^{-1} K^{-1} for $\Delta S^{\ddagger}$.

Results and discussion

Phosphines react rapidly and reversibly with enneacarbonylmethinyltricobalt clusters to give complexes of the type $YCCo_3(CO)_8L$ [2]:

$$YCCo_3(CO)_9 + L \xrightarrow{\text{hexane}} YCCo_3(CO)_8L + CO$$

However there are two constraints in a kinetic study of this system. First, some phosphines give more highly substituted products [2] and second, when Y is an alkyl group a structural rearrangement occurs to a bridged-carbonyl configuration [13] except when L is Ph_3P or Ph_3As. For these reasons and because our main interest was on the influence of Y, reactions with Ph_3P were most extensively studied.

The reactions were studied over the temperature range 308-338 K and the observed first-order rate constants are listed in Table 1. In all cases good first-order plots were obtained and, where studied, it can be seen that variation not only of ligand concentration but of ligand nucleophilicity produced no change in observed rate constants greater than experimental error. The evidence points strongly to a simple dissociative mechanism with no bimolecular term:

$$YCCo_3(CO)_9 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} YCCo_3(CO)_8 + CO$$

$$YCCo_3(CO)_8 + Ph_3P \xrightarrow{k_2} YCCo_3(CO)_8Ph_3P$$

Applying the steady-state assumption:

$$\text{rate} = k_1\ [YCCo_3(CO)_9]\ [Ph_3P]/(k_{-1}/k_2)[CO] + [PPh_3]$$

When (k_{-1}/k_2)[CO] is negligible (under a nitrogen flow or at the early part of the reaction) this reduces to the observed rate law. No rate inhibition in a CO atmosphere was noted indicating that k_{-1}/k_2 is small. Partial support for this suggestion came from a study [14] of the reverse reaction, the first order rate constants being a factor of ten smaller than those in Table 1. Intuitively, a dissociative mechanism is in keeping with the known chemical and structural behaviour of Co_3C clusters. The congested environment around each cobalt atom would make it difficult for a cluster to attain a bimolecular transition state.

High activation energies are also consistent with a dissociative mechanism and, when the large errors are taken into account, the $\Delta S^{\ddagger}$ values fall within the range found in comparable systems (Table 2). Some correlation might be expected between k_{obs} and E_a, the nature of the apical substituent and the Co—CO bond strength in the respective clusters. Carbonyl stretching frequencies suggest that the Co—CO bond strength decreases in the order Y = Ph ≈ Me > H > F (Table 2). The rationale is that inductive effects are transmitted through a delocalised Co_3C core and this order reflects a decrease in electron density at the cobalt atoms

TABLE 2

ACTIVATION PARAMETERS FOR REACTIONS WITH Ph_3P AND CARBONYL STRETCHING FREQUENCIES OF $YCCO_3(CO)_9$

Cluster	E_a (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ν(CO) (cm^{-1})			
$CH_3CCo_3(CO)_9$	102.1	−18.0	2101w	2051vs	2038s	2018s
$HCCo_3(CO)_9$	97.9	−35.1	2106w	2057.5vs	2041.5s	2023m
$C_6H_5CCo_3(CO)_9$	91.6	−40.2	2102m	2055vs	2041s	2021w
$FCCo_3(CO)_9$	89.1	−47.7	2110m	2062vs	2047s	2029m

[2,9]. Indeed the rate of ^{14}CO exchange does increase in the order [10] (F > H > Ph ≈ Me) as do the k_{obs} and E_a values reported herein, apart from Y = Ph, although the range of E_a values is small. Other work [15] indicates that the phenyl ring acts as a $(+I)(-M)$ substituent to the cluster and it is conceivable that the $-M$ effect is increased in the transition state. Nonetheless the same argument should hold for ^{14}CO exchange and the fact that k_{obs} and E_a are approximately equal when Y = Ph and F must be regarded as anomalous.

In conclusion, phosphine substitution reactions of enneacarbonylmethinyltricobalt clusters proceed by the simple dissociative mechanism found in other cluster substitution reactions [16] and there is no evidence for a bimolecular term noted in reactions of more basic phosphines with $Ru_3(CO)_{12}$ [16]. The fact that the kinetic parameters vary with the nature of the apical substituent Y is strong support for delocalised model proposed for the Co_3C core.

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