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THE KINETICS OF THE MONOSUBSTITUTION REACTIONS BETWEEN PHOSPHINES AND ALLYLDICARBONYLNITROSYLIRON

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SUMMARY

The complexes [Fe(CO)(NO)(C_3H_5)(ligand)] (C_3H_5=allyl) have been prepared by treatment of $Fe(CO)_2(NO)C_3H_5$ with the following ligands: $P(n\text{-}C_4H_9)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$. $P(OC_4H_9)_3$, $P[OCH(CH_3)_2]_3$, $P(OCH_2)_3CCH_3$, $P(C_6H_5)_2Cl$, $P(OC_6H_5)_3$ and $P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$. The kinetics of these monosubstitution reactions have been examined, and indicate that they proceed through association between the starting complex and the ligand. No reaction occurs with pyridine, and the reaction with $As(C_6H_5)_3$ is slow. The results are consistent with the substrate being a class b or soft metal.

The rates are little affected by change in dielectric constant or coordinating ability of the solvent. For nucleophiles with the same ligand atom (phosphorus) the rates do not depend primarily on the basicity or polarizability of the reagents, but rather on their bulk.

INTRODUCTION

The monosubstitution reaction between phosphine ligands and $Co(CO)_3C_3H_5$ (C_3H_5=allyl) is thought to proceed by a dissociative-type mechanism, and the nucleophile has no appreciable influence on the rate[1]. Since the presence of NO rather than CO ligands in carbonylnitrosyl complexes favours the occurrence of parallel associative substitution paths[2], we have used the complex $Fe(CO)_2(NO)C_3H_5$ in a study of the effect of the entering ligand on the mechanism of substitution in complexes having the three-electron allylic group as substrate ligand. Such a study also gives information about the nature of the metal–allyl bond, and particularly about the difference between the behaviour of the allyl and NO ligands. For this work a series of monosubstituted derivatives, [Fe(CO)(NO)(C_3H_5)(phosphine)] have been prepared and characterized. The relative reactivity of $Fe(CO)_2(NO)C_3H_5$ towards nitrogen, phosphorus and arsenic ligands have also been established.

EXPERIMENTAL

Preparation and characterization of the complexes

(*a*). $Fe(CO)_2(NO)C_3H_5$

This complex has been prepared previously[3-5]. We used the reaction of

$NaFe(CO)_3NO$[6] with allyl chloride in ethereal solution at room temperature[3,5], which went to completion in a day. The sodium chloride was filtered off, and the filtrate was fractionally distilled under vacuum, the solution being kept at the temperature of the NaCl/water/ice eutectic until the ether and the residual allyl chloride had been removed. The complex was then distilled at room temperature to give a dark-red oil. Water and traces of $Fe(CO)_2(NO)_2$, were separated by distilling under a diffusion pump vacuum in the presence of P_2O_5; the first fraction contained all the $Fe(CO)_2(NO)_2$, and the second was the pure complex. It was identified by its CO and NO IR stretching frequencies (Table 1).

TABLE 1

ANALYTICAL DATA AND CARBONYL AND NITROSYL STRETCHING FREQUENCIES FOR COMPOUNDS $Fe(CO)(NO)(C_3H_5)$(LIGAND) IN TOLUENE

Ligand	Isolated as	M.p. (°C)	Analysis found (calcd.) (%) C	H	N	Mol. wt. found (calcd.)	ν(CO) (cm⁻¹)	ν(NO) (cm⁻¹)
CO	Dark red, liquid					193 (183)	2034, 1975	1745
$P(n\text{-}C_4H_9)_3$	Dark red, liquid		53.8 (53.15)	9.03 (8.84)	3.92 (3.92)		1926	1692
$[P(C_6H_5)_2CH_2]_2$	Orange, solid[a]	190[c]	58.20 (57.65)	4.86 (4.84)	3.93 (3.95)		1926	1692
	Orange, solid[b]	142–144	65.1 (65.08)	4.95 (5.28)	2.27 (2.53)			
$P(OCH_3)_3$	Dark red, liquid					260 (278.8)	1944	1710
$P(OC_2H_5)_3$	Dark red, liquid					310 (321.1)	1939	1703
$P(OC_4H_9)_3$	Dark red, liquid		51.2 (52.41)	8.04 (8.62)	3.72 (3.71)	360 (374.3)	1939	1703
$P[OCH(CH_3)_2]_3$	Dark red, liquid		42.99 (42.25)	7.22 (7..12)	3.47 (3.47)		1936	1702
$P(C_6H_5)_3$	Red, solid	173–174	63.33 (63.39)	4.83 (4.85)	3.36 (3.25)		1935	1700
$P(OCH_2)_3CCH_3$	Red, solid	155–158	34.31 (33.47)	4.72 (4.81)	4.79 (4.78)	364 (363.2)	1960	1722
$P(C_6H_5)_2Cl$	Dark red, liquid						1960	1725
$P(OC_6H_5)_3$	Dark red, solid	84–86	56.80 (55.50)	4.33 (4.50)	3.01 (2.88)	480 (465.2)	1958	1723
$As(C_6H_5)_3$							1929	1704

[a] Data for $[Fe(CO)(NO)(C_3H_5)_2P(C_6H_5)_2CH_2]_2$ complex. [b] Data for $Fe(CO)(NO)(C_3H_5)P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ complex. [c] Decomposition without melting.

(*b*). *Monosubstituted complexes*

(*b1*). *$Fe(CO)(NO)(C_3H_5)P(OCH_3)_3$, $Fe(CO)(NO)(C_3H_5)P(OC_2H_5)_3$, $Fe(CO)(NO)(C_3H_5)P(OC_4H_9)_3$, $Fe(CO)(NO)(C_3H_5)P(n\text{-}C_4H_9)_3$.* These complexes were obtained by mixing $Fe(CO)_2(NO)C_3H_5$ and the appropriate ligand in 1/0.9 amounts in ether at room temperature, except that for the $P(n\text{-}C_4H_9)_3$ toluene was used as solvent. The solution was dried, and the viscous red liquid was chromatographed on an alumina column using an 1/1 CH_2Cl_2/n-pentane mixture as eluent. The complexes were characterized by their IR spectra and molecular weights (see Table 1).

(b2). $Fe(CO)(NO)(C_3H_5)[P(OCH_2)_3CCH_3]$. Equimolar amounts of $Fe(CO)_2(NO)C_3H_5$ and of the ligand, prepared according ref. 7, were mixed at room temperature in diethyl ether; reaction was complete in 2 h. The solvent was evaporated and the solid recrystallized from CH_2Cl_2/n-pentane, to give red crystals, m.p. 155–158°. For the characteristics of the complex see Table 1.

(b3). $Fe(CO)(NO)(C_3H_5)P[OCH(CH_3)_2]_3$, $Fe(CO)(NO)(C_3H_5)P(OC_6H_5)_3$, $Fe(CO)(NO)(C_3H_5)P(C_6H_5)_3$. These complexes were obtained by treating equimolar amounts of $Fe(CO)_2(NO)C_3H_5$ and of the appropriate ligand in toluene at 50° for two days. The first complex is a viscous liquid and was purified as in (*b*1) above. The others are solid, and were purified by crystallization from CH_2Cl_2/n-pentane; the dark-red crystals had m.p.'s of 84–86° and 173–174° (lit. 174°[4]) respectively. For the characteristics of the complexes see Table 1.

(b4). $[Fe(CO)(NO)P(C_6H_5)_2CH_2]_2$ *and* $Fe(CO)(NO)(C_3H_5)P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$. $[Fe(CO)(NO)(C_3H_5)P(C_6H_5)_2CH_2]_2$ was prepared by treating $Fe(CO)_2(NO)C_3H_5$ and the ligand $P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ (see ref. 8) in 2/1 molar amounts in toluene at room temperature. After evaporation of the solvent the residue was washed with acetone to eliminate the excess of ligand and recrystallized from CH_2Cl_2/n-pentane. It is soluble in CH_2Cl_2, but much less so in the common organic solvents; it decomposes at 190° without melting. It was characterized by analysis and IR spectrum (Table 1).

Treatment of $Fe(CO)_2(NO)C_3H_5$ with $P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ ($\frac{1}{4}$ molar ratio) in toluene at room temperature gave $Fe(CO)(NO)(C_3H_5)P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$. This compound is soluble in all the common organic solvents. It was separated from the excess of ligand by extraction with acetone, which readily dissolves the complex but not the ligand. The residue obtained after evaporation of acetone, was crystallized from CH_2Cl_2/n-pentane; m.p. 142–144°; for its characteristics see Table 1.

During the kinetic work in which the complex ligand ratio was $>1/10$, $Fe(CO)(NO)(C_3H_5)PPh_2CH_2CH_2PPh_2$ was obtained.

(b5). $Fe(CO)(NO)(C_3H_5)P(C_6H_5)_2Cl$. This was prepared as described for the $P(C_6H_5)_3$ derivative from $Fe(CO)_2(NO)C_3H_5$ and the appropriate ligand. The dark-red liquid could not be purified owing to its easy decomposition. It was identified from its IR spectrum (see Table 1).

(b6). Reaction with $As(C_6H_5)_3$. While nitrogen ligands (pyridine) caused decomposition of the complex, with $As(C_6H_5)_3$ in toluene at 60–70° bands characteristic of the monosubstituted derivative initially appeared (see Table 1); however their intensity did not increase with time, while that of the bands of $Fe(CO)_2(NO)C_3H_5$ decreased; this indicates that there was a gradual decomposition of the monosubstituted complex.

(c). Disubstitution reactions

The monosubstituted complexes were treated with an excess of the ligand in toluene at 90–100°. Even after 20 days no appreciable formation of disubstituted compounds was detected, even with the phosphite ligands which most readily bring about disubstitution[9].

Infrared spectra

The π-allylic structure of $Fe(CO)_2(NO)C_3H_5$ has been established from the NMR spectrum[5]. The IR spectrum confirms this structure: no bands are present in the 1600–1640 cm^{-1} range corresponding to the C=C stretchings of organic allylic compounds[10]; instead there is a band at 1495 cm^{-1}, assigned to the C–C stretching of the π-allylic ligand[11]. This band is present with all the monosubstituted complexes, and is within 10 cm^{-1} of the above value. The CO and NO stretching frequencies of $Fe(CO)_2(NO)C_3H_5$ and its derivatives are listed in Table 1.

A comparison of the CO frequencies of $Fe(CO)_2(NO)_2$[12] and of $Fe(CO)_2(NO)C_3H_5$ reveals a remarkable frequency lowering in the allylic complex [$Fe(CO)_2(NO)_2$ 2090, 2040 cm^{-1}, $Fe(CO)_2(NO)C_3H_5$ 2034, 1975 cm^{-1}]; this reflects an increased electronic charge to the metal, due to the lower π-acceptor ability of the π-allylic ligand with respect to the NO ligand. This is supported also by the rate constant values for monosubstitution with these two complexes (see ref. 12 and the present work). The effects of the phosphine ligands on the CO and NO stretching frequencies are consistent with those found with other carbonyl and carbonylnitrosyl complexes[13].

Conditions of the kinetic work

The toluene and cyclohexane solvents were refluxed over Na and distilled under nitrogen; tetrahydrofuran (THF) was treated with KOH pellets in the presence of benzoquinone and distilled over Na[14]. Reproducible kinetic runs could only be obtained with THF when the solvent was freshly distilled. The runs were performed under nitrogen. The liquid ligands were commercial products, distilled before use; $P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ was prepared according ref. 8, $P(OCH_2)_3CCH_3$ according ref. 7.

The kinetics, when sufficiently slow, were performed in dark sealed ampoules. Faster runs were carried out in small flasks from which samples were removed by syringe. The kinetic runs were followed with a Perkin–Elmer mod. 337 IR spectrophotometer, the disappearance of the higher frequency CO stretching band of $Fe(CO)_2(NO)C_3H_5$ and, whenever possible, the appearance of the CO band of the monosubstituted complex being recorded; when both CO bands could be used, the separate rate constants agreed within experimental error.

0.1 mm and 0.5 mm NaCl cells were employed when the complex concentration was $\sim 2\times10^{-2}$ mole·l^{-1} and $\sim 5\times10^{-3}$ mole·l^{-1} respectively. At high ligand concentrations, a solution containing the ligand was used as reference. The $Fe(CO)_2(NO)C_3H_5$ was stable only for a few hours in the absence of ligands, but it was stable in the presence of ligands, as shown by the absorbancy values of the final products of the kinetic runs, which agreed with those of solutions containing the same concentration of separately prepared monosubstituted complex.

The kinetics were performed at 50°; for the activation parameter measurements temperatures of 25, 35, 40 and 45° were also used. The $\Delta E^{\neq}$ values are accurate to about ±1 kcal/mole. The reactions were followed from about 30% to 80% completion depending on their rates. They went to completion in all cases. Under a CO atmosphere it was possible to follow a small part of the inverse reaction of ligand replacement by CO with the complex $Fe(CO)(NO)(C_3H_5)P(OC_6H_5)_3$.

RESULTS AND DISCUSSION

Table 2 gives the second-order rate constant values for the reaction with $P(C_6H_5)_3$ at different temperatures in toluene, cyclohexane and THF, and Table 3 those in toluene for the reactions with $P(OC_2H_5)_3$ and $P(C_6H_5)_2CH_2CH_2P(C_2H_5)_2$. Table 4 reports the k_2 values for all other ligands at 50°. The mean k_2 values at 50° are listed in Table 5 along with Streuli's ΔHNP values for the ligands concerned[15]. Table 5 gives also some activation parameters.

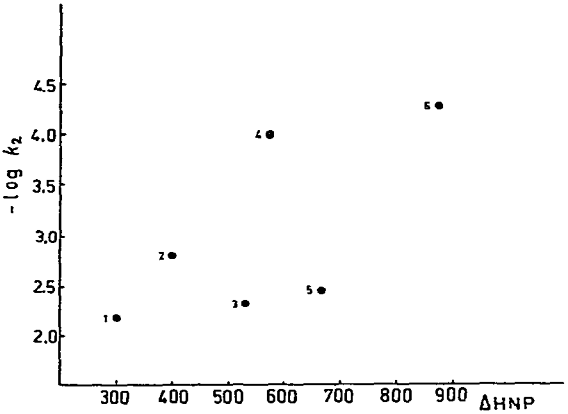

Fig. 1

Fig. 1. The relationship between the rate of reaction and the basicity of the nucleophile (ΔHNP) for the reaction of $Fe(CO)_2(NO)C_3H_5$ with (1) $P(n\text{-}C_4H_9)_3$, (2) $P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$, (3) $P(OCH_3)$, $P(OC_2H_5)_3$, $P(OC_4H_9)_3$, $P[OCH(CH_3)_2]_3$, (4) $P(C_6H_5)_3$, (5) $P(OCH_2)_3CCH_3$, (6) $P(OC_6H_5)_3$.

For all the phosphine and phosphite ligands used, the kinetics were first-order in the complex and in the entering ligand. The most likely mechanism is an associative one, involving a pentacoordinated transition complex, as proposed for the complexes $Co(CO)_3NO$[2,16,17] and $Fe(CO)_2(NO)_2$[17,18], which are isoelectronic with the allylic complex.

Two items of evidence support this mechanism:

(1). The relatively low activation energies recorded in toluene (Table 5) agree with those observed in associative mechanisms[16] in which breaking of the metal–carbon bond is relatively unimportant in the transition complex; the negative activation entropies reflect a decrease in the degrees of freedom on going to the transition complex, as required for an associative path.

(2). The solvent effects for the kinetics with the $P(C_6H_5)_3$ ligand (see Table 2) are typical of an associative mechanism. In contrast with the cases of $Co(CO)_3NO$[17] and $Fe(CO)_2(NO)_2$[18], for which coordinating solvents like THF, CH_3CN and CH_3OH change the reaction mechanism from a dissociative one to one involving association with the solvent, followed by substitution of the solvent with the phosphine ligand, the solvent does not have any appreciable influence on the mechanism (see Table 2), even in THF, a solvent of high coordinating power.

The $Co(CO)_3C_3H_5$ complex[1], isoelectronic with the one under study, undergoes monosubstitution by a dissociative type mechanism; thus in the allylic isoelectro-

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TABLE 2

SECOND-ORDER RATE CONSTANTS (k_2) FOR THE REACTION $Fe(CO)_2(NO)C_3H_5 + P(C_6H_5)_3 \rightarrow Fe(CO)(NO)(C_3H_5)P(C_6H_5)_3 + CO$ IN VARIOUS SOLVENTS

Complex concentration $\sim 2 \times 10^{-2}$ mole·l^{-1}.

[L] (mole·l^{-1})	$10^5 \times k_2$ (l·mole^{-1}·sec^{-1})	[L] (mole·l^{-1})	$10^5 \times k_2$ (l·mole^{-1}·sec^{-1})
In toluene at 40°		*In toluene at 50°*	
0.5011	4.50	0.2403	9.49
0.5006	4.19	0.5272	10.30
0.7510	4.19	0.7501	9.97
1.0000	4.56	1.0010	10.01
In toluene at 45°		*In cyclohexane at 50°*	
0.1001	6.96	0.1519	12.30
0.2455	6.64	0.2192	13.0
0.2500	6.28	0.5009	12.5
0.2519	6.50	0.7309	11.5
0.4959	6.79		
0.5090	6.34	*In tetrahydrofuran at 50°*	
0.7494	6.67	0.2496	9.90
0.7502	6.45	0.4992	9.80
0.9856	6.71	0.4995	10.2
		0.7496	10.1
		0.7509	9.6

TABLE 3

SECOND-ORDER RATE CONSTANTS (k_2) FOR THE REACTIONS $Fe(CO)_2(NO)C_3H_5 + L \rightarrow Fe(CO)(NO)(C_3H_5)L + CO$ IN TOLUENE; $L = P(OC_2H_5)_3$ AND $P(C_6H_5)CH_2CH_2P(C_6H_5)_3$

Complex concentration $\sim 5 \times 10^{-3}$ mole·l^{-1}.

Temp. (°C)	[L] (mole·l^{-1})	$10^3 \times k_2$ (l·mole^{-1}·sec^{-1})
$L = P(OC_2H_5)_3$		
25	0.1006	0.76
25	0.3013	0.79
35	0.1098	1.49
40	1.1024	2.18
50	0.0511	4.93
50	0.0524	4.75
50	0.0810	4.55
50	0.0976	4.56
$L = P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$		
40	0.0626	0.69
40	0.0817	0.76
40	0.1014	0.75
40	0.1619	0.73
50	0.0617	1.63
50	0.07997	1.63
50	0.0998	1.57
50	0.1605	1.51

TABLE 4

SECOND-ORDER RATE CONSTANTS (k_2) FOR THE REACTIONS $Fe(CO)_2(NO)C_3H_5 + L \rightarrow Fe(CO)(NO)(C_3H_5)L + CO$ AT 50.0° IN TOLUENE

Complex concentrations ~5×10^{-3} mole·l^{-1}; for L = $P(OC_6H_5)_3$ and $P(C_6H_5)_2Cl$ 2×10^{-3} mole·l^{-1}.

[L] (mole·l^{-1})	$10^5 \times k_2$ (l·mole^{-1}·sec^{-1})	[L] (mole·l^{-1})	$10^5 \times k_2$ (l·mole^{-1}·sec^{-1})
L = $P(n\text{-}C_4H_9)_3$		*L = $P(OCH_2)_3CCH_3$*	
0.0303	667	0.0531	369
0.0319	624	0.0798	357
0.0508	648	0.1138	351
0.0745	737	0.2087	387
0.0754	724		
L = $P(OCH_3)_3$		*L = $P(C_6H_5)_2Cl$*	
0.02997	421	0.0752	9.9
0.0563	451	0.2545	10.2
0.0587	457	0.5034	10.0
0.0761	416	1.0040	10.5
0.0975	423		
L = $P(OC_4H_9)_3$		*L = $P(OC_6H_5)_3$*	
0.0259	510	0.5405	5.18
0.0540	468	0.7655	4.97
0.0739	538	0.9951	5.10
0.0990	508		
L = $P[OCH(CH_3)_2]_3$			
0.0273	215		
0.0588	202		
0.0799	210		
0.1101	202		

TABLE 5

MEAN SECOND-ORDER RATE CONSTANTS (k_2) FOR THE REACTIONS $Fe(CO)_2(NO)C_3H_5 + L \rightarrow Fe(CO)(NO)(C_3H_5)L + CO$ AT 50° IN TOLUENE

ΔHNP = basicity values according Streuli[15].

Ligand	$10^5 \times k_2$ (l·mol^{-1}·sec^{-1})	ΔHNP	$\Delta E^{\neq}$ (kcal·mole^{-1})	$\Delta S^{\neq}$ (e.u.)
$P(n\text{-}C_4H_9)_3$	680	300		
$P(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$	159	400	15.4	−26
$P(OCH_3)_3$	434	520[a]		
$P(OC_2H_5)_3$	477	520[a]	14.0	−28
$P(OC_4H_9)_3$	506	520[a]		
$P[OCH(CH_3)_2]_3$	207	520[a]		
$P(C_6H_5)_3$	9.94	573	15.5	−31
$P(OCH_2)_3CCH_3$	366	665		
$P(C_6H_5)_2Cl$	10.2			
$P(OC_6H_5)_3$	5.08	875		

[a] Values from ref. 12.

nic series the introduction of NO in place of CO groupings gradually shifts the reaction mechanism from a dissociative to an associative one, as shown by the series $Ni(CO)_4$[19], $Co(CO)_3NO$[2,16], $Fe(CO)_2(NO)_2$[12,18]. Possible reasons for this change of mechanism are discussed in ref. 2.

The rate constants found for the iron allylic complex are lower than those for $Fe(CO)_2(NO)_2$ at the same temperature. This corresponds, to a lowered π-bonding ability of the π-allylic ligand with respect to the NO grouping in agreement with the IR evidence; the increase in the electronic charge to the central metal lowers the rate of the associative mechanism.

The ligands used were chosen to cover a range of ΔHNP basicity values (see Table 5) wide enough to show the influence of ligand basicity and/or polarizability prevails in the reaction kinetics, giving rise to linear log k_2 *vs.* ΔHNP plots as found for other carbonyl and carbonylnitrosyl complexes[2,12,20]. It is apparent from Fig. 1 that there is no such linear dependance in the reaction under study.

A comparison of the rate constant ratios for reaction with the $P(C_6H_5)_3$ and $P(OC_4H_9)_3$ ligands in $Fe(CO)_2(NO)_2$ and $Fe(CO)_2NOC_3H_5$, *viz.* $Fe(CO)_2(NO)_2$, $k_{P(C_6H_5)_3}/k_{P(OC_4H_9)_3} = 1/6.6$; $Fe(CO)_2(NO)C_3H_5$, $k_{P(C_6H_5)_3}/k_{P(OC_4H_9)_3} = 1/52$, clearly indicates a marked difference of behaviour between phosphines and phosphites in the reaction, in that, for the same relative basicity, the phosphite ligands react about fifteen times faster with the $Fe(CO)_2(NO)C_3H_5$ substrate than with the isoelectronic $Fe(CO)_2(NO)_2$ one. This result can be understood in terms of the substantial steric effect exerted by the π-allylic substrate ligand; the less bulky phosphites react much faster than the phosphine ligands with the bulky $Fe(CO)_2$-$(NO)C_3H_5$ substrate, the effect being particularly marked in the case of the compact $P(OCH_2)_3CCH_3$ ligand. Among the phosphines, the bulkier $P(C_6H_5)_3$ ligand reacts particularly slowly for its basicity. Such a steric influence on reaction rate was noted by Basolo *et al.*[20] in the monosubstitution reactions of the complex $C_5H_5Rh(CO)_2$ with which the $P(C_6H_{11})_3$ ligand reacted very slowly in spite of its high basicity.

Nitrogen ligands do not react at all with the $Fe(CO)_2(NO)C_3H_5$ substrate, while the $As(C_6H_5)_3$ ligand reacts much more slowly than the phosphine ligands; the relative order of reactivity, *viz.* $N \ll P \gg As$, is that expected for a soft reaction center[21,22].

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