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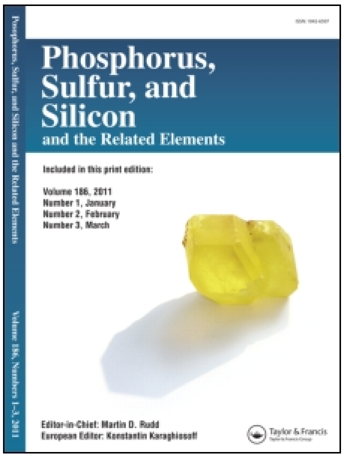

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Substitution Reactions of Potassium Tetracarbonylhydridoferrate with Phosphanes. Effect of the Stereoelectronic Properties of the Phosphane

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Substitution Reactions of Potassium Tetracarbonylhydridoferrate with Phosphanes. Effect of the Stereoelectronic Properties of the Phosphane.

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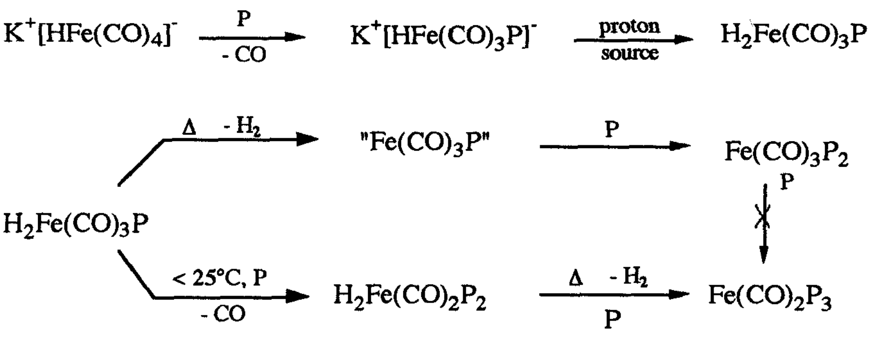
Introduction

Ligand substitutions on transition metal complexes have attracted much attention, both for the synthesis of new heteroleptic complexes and for the study of reaction mechanisms.[1] In this respect, carbonyl metals have been particularly studied.[2] The reaction mechanisms that have been evidenced, or proposed, are of the same type as those involved in classical organic chemistry for the nucleophilic substitutions at carbon. These studies, however, are limited to neutral transition metal carbonyl complexes. To the best of our knowledge, the only reported substitution reaction on an anionic transition metal carbonyl complex concerns the reaction of phosphanes or activated alkenes with $[Co(CO)_4]^-$.[3]

As part of our interest [4] in developing new synthetic applications of $[HFe(CO)_4]^-$, we have studied the reaction of $KHFe(CO)_4$, **1**, with phosphanes.[5,6] This reaction is a very efficient method for the synthesis of various substituted hydridoironcarbonyl derivatives among which the hydridoanions $K^+[HFe(CO)_3\{P(OR)_3\}]^-$ and the dihydrides $H_2Fe(CO)_2(PR_3)_2$ (PR_3= $P(n\text{-}Bu)_3$, PMe_2Ph, $P(OMe)_3$, $P(OEt)_3$ and $P(OPh)_3$). In this paper, we compare the reactivity of various phosphanes with **1** to obtain information about the influence of their stereoelectronic properties in substitution reactions on an anionic, 18-electron complex.

Results and discussion

The generalized reaction pathway (scheme 1) for the reaction of **1** with phosphanes has been established on the basis of experiments conducted under various conditions.[5,6]



Scheme 1 (P= phosphine or phosphite)

7

Phosphane	θ [a]	pK_a [a]	Reaction time (h) [b]	Product	Yield % (isolated)
$P(OMe)_3$	107	2.60	1	$K^+[HFe(CO)_3\{P(OMe)_3\}]^-$	91
$P(OEt)_3$	109	3.35	1	$K^+[HFe(CO)_3\{P(OEt)_3\}]^-$	97
PMe_2Ph	122	6.49	no significant reaction after 24 h		
$P(OPh)_3$	128	-1.20	2	$K^+[HFe(CO)_3\{P(OPh)_3\}]^-$	98
$P(n\text{-}Bu)_3$	132	8.43	no significant reaction after 24 h		
PPh_3	145	2.73	no significant reaction after 24 h		
PCy_3	170	9.70	no significant reaction after 24 h		

b

In protic medium (H_2O-THF), the reaction leads directly to the dihydrides $H_2Fe(CO)_2P_2$, and it is not possible to observe the hydridocomplex $K^+[HFe(CO)_3P]^-$. It has been found, however, that protonation of the latter, and ligand substitution on $H_2Fe(CO)_3P$ are very fast. Hence, the first ligand substitution on **1** is the rate-determining step, and reaction times given in Table 2 are a good reflection on the order of reactivity. As may be seen, the reactivity of phosphanes is clearly determined by their cone angle. However, in contrast to what was observed in THF, their basicity does not appear to be a determining parameter. Indeed, the poorly basic $P(OPh)_3$ and the highly basic $P(n\text{-}Bu)_3$, which exhibit comparable cone angles, react in a similar manner whereas $P(OMe)_3$ and PPh_3, which exhibit similar pK_a values but different cone angles react in a dramatically different manner.

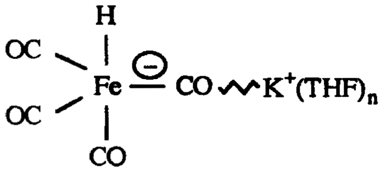
Phosphane	θ [b]	pK_a [b]	Reaction time (h)	Product	Yield % (isolated)
$P(OMe)_3$	107	2.60	1	$H_2Fe(CO)_2[P(OMe)_3]_2$	90
$P(OEt)_3$	109	3.35	1	$H_2Fe(CO)_2[P(OEt)_3]_2$	91
PMe_2Ph	122	6.49	20	$H_2Fe(CO)_2(PMe_2Ph)_2$	60[d]
$P(OPh)_3$	128	-1.20	24	$H_2Fe(CO)_2[P(OPh)_3]_2$	94
P(*n*-Bu)$_3$	132	8.43	24	$H_2Fe(CO)_2$[P(*n*-Bu)$_3$]$_2$	81
PPh_3	145	2.73	no significant reaction after 48 h		
PCy_3	170	9.70	no significant reaction after 48 h		

The IR spectra of $M^+[HFe(CO)_4]^-$ in THF have been thoroughly studied by Darensbourg *et al.* [9] When M^+ is Na^+, an interaction has been evidenced between the latter and an equatorial carbon monoxide ligand. This interaction, which gives rise to a ν_{CO} absorption band at 1854 cm^{-1} is believed to make the axial carbon monoxide ligand more labile. In contrast, when the cation is PPN^+, this interaction no longer occurs, and the complex is much more resistant than $Na^+[HFe(CO)_4]^-$ to ligand exchange with ^{13}CO.[9]

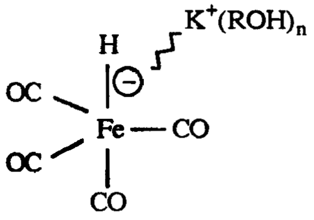
Solutions of **1** in THF exhibit the same characteristic interaction (ν_{CO} = 1856 cm^{-1}) whereas solutions in protic medium do not. Thus, it could be expected that CO substitution on **1** would be easier in THF than in protic media. In fact, the reverse is observed for P(*n*-Bu)$_3$ and PMe_2Ph. Actually, in methanol or ethanol, all the IR carbonyl absorption bands of **1** are shifted to higher values (Table 3). The Fe-CO bond is weaker and hence, CO substitution is more facile in these solvents as compared to THF.

solvent	IR: ν_{CO}(cm^{-1})	^{1}H NMR: δ(ppm)
THF	1999 (w); 1911 (sh); 1878 (S); 1856 (sh)	- 8.75 (THF-d_8)
MeOH or EtOH	2008 (w); 1921 (sh); 1893 (S)	- 9.05 (CD_3OD)

This observation means that the back-bonding on the carbonyl ligands for **1** in protic medium is less important than in THF and suggests an interaction between K^+ and the charge on the $[Fe\text{-}H]^-$. We were thus led to study the ^1H NMR spectra of **1** in order to compare its hydride chemical shifts in CD_3OH and in THF-d_8. As may be seen from Table 3, the hydridic character is more pronounced in methanol, and this observation led us to propose the following representations for **1** in THF (**1a**) and in protic medium (**1b**).



1a



1b

In **1b**, the withdrawing of the negative charge by $K^+(ROH)_n$ is more pronounced than in **1a** (IR data). Under these conditions, the carbon monoxide ligands are more labile, and the approach of the phosphane depends only on its cone angle. In contrast, in aprotic medium (**1a**), a higher charge density is present on the iron atom, and the approach of the phosphane is governed by both its cone angle and its basicity. For a given cone angle, the phosphane exhibiting the higher π-accepting properties reacts the more easily.

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