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Inorganica Chimica Acta 360 (2007) 2464–2470
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Electron-transfer chain catalysis in phosphine replacement reaction: Determination of relative donor capability of arylpyridylphosphines

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Received 16 August 2006; received in revised form 4 December 2006; accepted 8 December 2006
Available online 20 January 2007

Abstract

The slight differences in the donor capabilities of PPh_nPy_{3-n} ($n = 0$–3) could be measured directly in the equilibrium of phosphine replacement reaction on $(\eta^5\text{-}C_5H_5)Fe(CO)_2$-phosphine complexes, taking advantage of the radical pathway to establish equilibrium rapidly. The simultaneous determination of equilibrium constants is done in a single experiment. The donor capability increases in the order $PPh_3 < PPh_2Py < PPhPy_2 < PPy_3$ with quantified $(\eta^5\text{-}C_5H_5)Fe(CO)_2^+$-affinity scales at 1, 4.90, 11.0, and 20.3, respectively.

Keywords: Electron-transfer chain catalysis; Arylpyridylphosphines; Iron complexes; Radical process; Phosphine exchange; Cyclic voltammetry

1. Introduction

Organophosphines are used in many metal mediated reactions [1]. As a consequence, chemists have been interested in deducing their stereo-electronic properties [2], among which the best known parameters are the cone angle Θ and the electronic parameter χ by Tolman [3]. Also a good parameter, the pK_a value for HPR_3^+ depends on the interaction between the phosphorus and H^+, a hard acid [4]. Such an interaction is generally considered not the same as that between the phosphorus ligand and a low valent metal center in an organometallic complex. Derived from the IR data for $LNi(CO)_3$ (L = phosphorus ligand), the χ values reflect a combined property of both σ-donor and π-acceptor [3]. Many other evaluations have been attempted using IR [5], NMR [6], UV/Vis [7], Photoelectron [8], and Mössbauer spectroscopy [9], as well as theoretical [10], and electrochemical [11] methods and X-ray crystallography [12].

Giering et al. reported in their quantitative analysis of ligand effects, a series of phosphines with Θ, pK_a, χ, ν_{CO} and E° values were tabulated. In particular, the ν_{CO} and E° values were obtained from the iron-complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(L)C(O)Me$ and $(\eta^5\text{–}MeC_5H_4)Fe(CO)(L)\text{-}C(O)Me$, where L is a phosphorus ligand [13]. For the following triarylphosphines with $\Theta = 145°$, e.g., $P(p\text{-}C_6H_4NMe_2)_3$, $P(p\text{-}C_6H_4OPh)_3$, $P(p\text{-}C_6H_4Me)_3$, PPh_3, $P(p\text{-}C_6H_4F)_3$, $P(p\text{-}C_6H_4Cl)_3$, $P(p\text{-}C_6H_4CF_3)_3$, a decrease of ligand donor capability was clearly evident and there was a nice correlation among the parameters.

The series of arylpyridylphosphines PPh_nPy_{3-n} ($n = 0$–3) are also with Θ values approximately 145°, yet without readily available pK_a, χ, ν_{CO} and E° values for the evaluation of their donor capability. The only starting point is that the ^{31}P NMR chemical shifts are more upfield with more Ph-groups (δ −0.6, −1.9, −3.2, and −4.7 with increasing number of Ph-groups), a fact not necessarily translated into increasing donor capability, however. As there are slight differences in the donor capabilities of PPh_nPy_{3-n}, we have found that the direct measurement of an equilibrium

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doi:10.1016/j.ica.2006.12.051

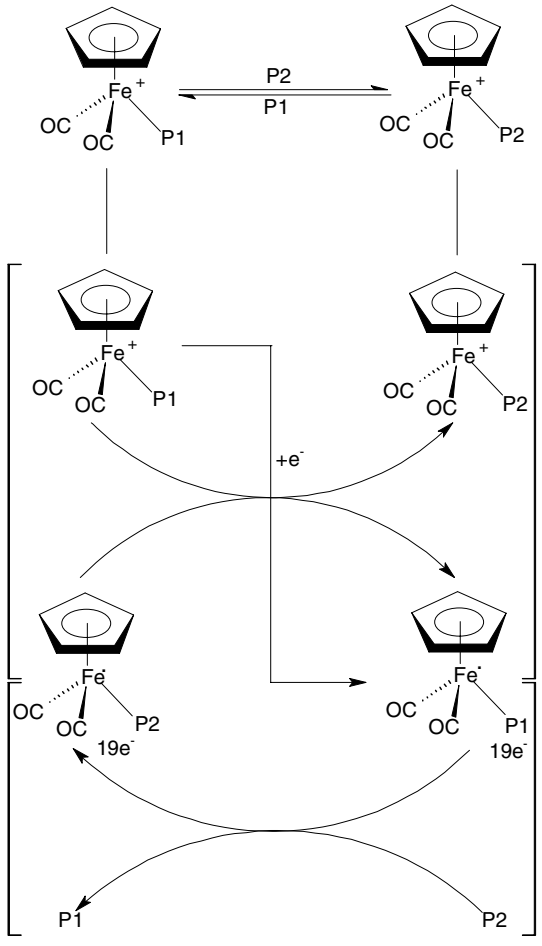
constant in the phosphine replacement reaction on (η^5-C_5H_5)$Fe(CO)_2$-phosphine complex is possible, taking advantage of the radical pathway to establish equilibrium rapidly. A simultaneous determination of equilibrium constants is also likely so that their donor capabilities could be compared in a single experiment.

1.1. Radical process

Pioneered by Rich and Taube in inorganic chemistry [14], the electron-transfer chain catalysis (ETC) is applied to the preparation of organometallic complexes, utilizing the greatly enhanced reactivity of organometallic 17e and 19e radicals in comparison to their 16e and 18e analogues [15–17]. The PPh_3 substitution for CO on [(η^5-C_5H_5)$Fe(CO)_3^+$] proceeds with 17e–19e pathway after electrochemical or chemical initiation, for instance, and yields [(η^5-C_5H_5)$Fe(CO)_2PR_3^+$] quantitatively [18]. The reaction of 1:1 (η^5-C_5H_5)$Fe(CO)_2I$/PPh_3 in THF at −78 °C, initialized by the addition of a small amount of reducing agents, e.g., diluted RLi [19] or (η^5-C_5H_5)$_2Co$, also follows the 17e–19e pathway and gives quantitative precipitates of [(η^5-C_5H_5)$Fe(CO)_2(PPh_3)^+$][I^-] instantaneously, I^- being selectively replaced by PPh_3 [20]. The anion [I^-] could be exchanged into [PF_6^-] without difficulty.

With easily available [(η^5-C_5H_5)$Fe(CO)_2(PPh_3)^+$][PF_6^-], the 17e–19e pathway enables one to instantly differentiate an incoming PPh_nPy_{3-n} replacement for PPh_3 on [(η^5-C_5H_5)$Fe(CO)_2PPh_3^+$]. Scheme 1 shows such an ETC reaction, the equilibrium constant K of Eq. (1) being the product of K_{redox} of Eq. (2) and $K_{exchange}$ of Eq. (3). The former is the coupling between the reduction of (η^5-C_5H_5)$Fe(CO)_2P1^+$ cation to (η^5-C_5H_5)$Fe(CO)_2P1^{\cdot}$ radical and the oxidation of (η^5-C_5H_5)$Fe(CO)_2P2^{\cdot}$ radical to (η^5-C_5H_5)$Fe(CO)_2P2^+$ cation. The latter is the coupling between an association of P2 with (η^5-C_5H_5)$Fe(CO)_2^{\cdot}$ radical to form (η^5-C_5H_5)$Fe(CO)_2P2^{\cdot}$ radical and a dissociation of (η^5-C_5H_5)$Fe(CO)_2P1^{\cdot}$ radical to form P1 and (η^5-C_5H_5)$Fe(CO)_2^{\cdot}$ radical. Both redox and exchange are facile because of high energy radical process in nature [15].

The following is a qualitative analysis on the K_{redox}. If P2 is a better donor than P1, the Fe atom of (η^5-C_5H_5)$Fe(CO)_2P2^{\cdot}$ radical has a higher electron density than that of (η^5-C_5H_5)$Fe(CO)_2P1^{\cdot}$ radical, i.e., the (η^5-C_5H_5)$Fe(CO)_2P2^{\cdot}$ radical is likely to be a better reductant than the (η^5-C_5H_5)$Fe(CO)_2P1^{\cdot}$ radical and one would expect that the K_{redox} for Eq. (2) must be greater than 1. On the other hand, $K_{exchange}$ could also be analyzed in a qualitative way with Eq. (3) envisioned as P1 and P2 in competition for the



$$K = \frac{[(\eta^5\text{-}C_5H_5)Fe(CO)_2P2^+][P1]}{[(\eta^5\text{-}C_5H_5)Fe(CO)_2P1^+][P2]} \quad \text{(Eq. 1)}$$

$$\rightleftharpoons \frac{[(\eta^5\text{-}C_5H_5)Fe(CO)_2P1^+] + [(\eta^5\text{-}C_5H_5)Fe(CO)_2P2^{\cdot}]}{[(\eta^5\text{-}C_5H_5)Fe(CO)_2P1^{\cdot}] + [(\eta^5\text{-}C_5H_5)Fe(CO)_2P2^+]}$$

$$K_{redox} = \frac{[(\eta^5\text{-}C_5H_5)Fe(CO)_2P1^{\cdot}][(\eta^5\text{-}C_5H_5)Fe(CO)_2P2^+]}{[(\eta^5\text{-}C_5H_5)Fe(CO)_2P1^+][(\eta^5\text{-}C_5H_5)Fe(CO)_2P2^{\cdot}]} \quad \text{(Eq. 2)}$$

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2P1^{\cdot}] + P2 \rightleftharpoons P1 + [(\eta^5\text{-}C_5H_5)Fe(CO)_2P2^{\cdot}]$$

$$K_{exchange} = \frac{[P1][(\eta^5\text{-}C_5H_5)Fe(CO)_2P2^{\cdot}]}{[(\eta^5\text{-}C_5H_5)Fe(CO)_2P1^{\cdot}][P2]} \quad \text{(Eq. 3)}$$

Scheme 1. Phosphine exchange reaction with an electron-transfer chain catalytic pathway.

same $[(\eta^5\text{-}C_5H_5)Fe(CO)_2^{\cdot}$ radical. If P2 is a better donor than P1, the $(\eta^5\text{-}C_5H_5)Fe(CO)_2^{\cdot}$ radical would prefer a ligation with P2 to a ligation with P1 and one would also expect that the $K_{exchange}$ of Eq. (3) must be greater than 1. These overall effects of a favoring phosphine substitution on the thermodynamic side combined with a rapid radical process on the dynamic side lead us to study the small difference among $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_n\ Py_{3-n}{}^+]$ by a simple ^{31}P NMR technique, namely, the intensity integration ratio.

2. Experimental

2.1. General

All manipulations were performed under an atmosphere of prepurified nitrogen with standard Schlenk techniques. All solvents were distilled from an appropriate drying agent [21]. Infrared spectra were recorded in CH_2Cl_2 using CaF_2 optics on a Perkin–Elmer 852 spectrophotometer. The ^1H NMR and ^{13}C NMR spectra were obtained on Bruker AC200/AC300 spectrometers, with chemical shifts reported in δ values, downfield positive, relative to the residual solvent resonance of $CDCl_3$ (^1H δ 7.24, ^{13}C δ 77.0). The ^{31}P NMR spectra were obtained on Bruker AC200/AC300 spectrophotometer using 85% H_3PO_4 as an external standard (δ 0.00). The melting points were determined on a Yanaco MPL melting-point apparatus and uncorrected. $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ [22], $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ [23], PPh_2Py [24], $PPhPy_2$ [25], PPy_3 [25], $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}PPh_3{}^+][PF_6{}^-]$ [20,26] and $(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me(PPh_3)$ [27] were prepared according to the literature procedure. Other reagents were obtained from commercial sources and used without further purification.

2.2. Preparation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L^+][PF_6{}^-]$, $L = PPh_2Py,\ PPhPy_2,\ PPy_3$

The procedures are the same for all PPh_nPy_{3-n}, following the preparation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3{}^+][PF_6{}^-]$ in the literature [20]. Only L = PPh_2Py is shown here as a routine run. $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (0.86 g, 2.83 mmol) and PPh_2Py (0.74 g, 2.83 mmol) were completely dissolved in THF (30 mL) and maintained at −78° C. A yellow precipitate appeared on addition of a trace amount of *n*-BuLi (1.6 M in hexane, 2 drops) to the solution. The solution was further stirred for 15 min before being gradually warmed up to room temperature. After filtration and washing with Et_2O for several times, the precipitate together with excess NH_4PF_6 was redissolved in CH_3CN with vigorous stirring. Addition of sufficient H_2O gave precipitates which were filtered and then washed with H_2O and Et_2O to produce $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_2Py^+][PF_6{}^-]$. For $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPhPy_2{}^+][PF_6{}^-]$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (0.54 g, 1.78 mmol), $PPhPy_2$ (0.47 g, 1.78 mmol), THF (26 mL) and for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPy_3{}^+][PF_6{}^-]$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (0.313 g, 1.0 mmol), PPy_3 (0.266 g, 1.0 mmol), THF (12 mL).

2.2.1. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_2Py^+][PF_6{}^-]$

Yield: 1.24 g (78%); mp: 222–223 °C; IR (CH_2Cl_2): ν_{CO} 2062 (s), 2021(s) cm^{-1}; ^{31}P NMR (acetone-d_6): δ 70.8 (s), −143.1 (hep, $^1J_{PF} = 2829$ Hz); ^1H NMR (acetone-d_6): δ 8.94 (b, 1H, Py), 7.46–7.96 (m, 13H, Ph and Py), 5.57 (b, 5H, Cp); ^{13}C NMR (acetone-d_6): δ 210.39 (d, $^2J_{PC} = 25.67$ Hz, CO), 126.94–152.07 (m, Ph and Py), 89.28 (s, Cp); MS (*m*/*z*): 440 (M^+-PF_6). *Anal.* Calc. for $C_{24}H_{19}NFeO_2F_6P_2$: C, 49.23; H, 3.25; N, 2.39. Found: C, 49.09; H, 3.14; N, 2.05%.

2.2.2. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPhPy_2{}^+][PF_6{}^-]$

Yield: 0.94 g (90%); mp: 205–206 °C; IR (CH_2Cl_2): ν_{CO} 2063 (s), 2021 (s) cm^{-1}; ^{31}P NMR (acetone-d_6): δ 74.2 (s), −143.1 (hep, $^1J_{PF} = 2829$ Hz); ^1H NMR (acetone-d_6): δ 8.96 (d, 2H, $^3J_{PH} = 4.04$ Hz, Py), 7.42–7.99 (m, 11H, Ph and Py), 5.58 (b, 5H, Cp); ^{13}C NMR (acetone-d_6): δ 210.38 (d, $^2J_{PC} = 24.45$ Hz, CO), 127.00–155.98 (m, Ph and Py), 89.03 (s, Cp); MS (*m*/*z*): 442 (M^+-PF_6). *Anal.* Calc. for $C_{23}H_{18}N_2FeO_2F_6P_2$: C 47.10; H, 3.07; N, 4.78. Found: C, 46.33; H, 2.84; N, 4.36%.

2.2.3. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPy_3{}^+][PF_6{}^-]$

Yield: 0.45 g (77%); mp: 200–202 °C; IR (CH_2Cl_2): ν_{CO} 2061 (s), 2020 (s) cm^{-1}; ^{31}P NMR (acetone-d_6): δ 76.1 (s), −143.1 (hep, $^1J_{PF} = 2829$ Hz), ^1H NMR (acetone-d_6): δ 8.95 (b, 3H, Py) 7.51–7.98 (m, 9H, Py), 5.55 (b, 5H, Cp); ^{13}C NMR (acetone-d_6): δ 210.22 (d, $^2J_{PC} = 24.00$ Hz, CO), 127.00–155.75 (m, Py), 88.67 (s, Cp); MS (*m*/*z*): 443 (M^+-PF_6+1). *Anal.* Calc. for $C_{22}H_{17}N_3FeO_2F_6P_2$: C 44.97; H, 2.90; N, 7.16. Found: C, 44.73; H, 2.72; N, 6.84%.

2.3. Phosphine exchange under ETC conditions

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_nPy_{3-n}{}^+][PF_6{}^-]$ (0.45 mmol) and PPh_mPy_{3-m} (0.15 mmol × 3, $m = 0$–3, $m \neq n$) were completely dissolved in CH_3CN (1.5 mL) and transferred to a 10 mm co-axial NMR tube that has an inner tube filled with 0.30 mmol $PPh_3(O)$ in $CDCl_3$ (0.5 mL) for external reference ($\delta = 29.5$ in ^{31}P NMR spectra) and for use in locking of the magnetic field. The 3:1:1:1 intensity integration ratio for the cation and the free ligands was observed from the ^{31}P NMR spectra. A trace amount of $(\eta^5\text{-}C_5H_5)_2Co$ was then introduced to the solution in the NMR tube. The ^{31}P NMR spectrum was remeasured in which a total of eight peaks corresponding to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_mPy_{3-m}{}^+]$ and PPh_nPy_{3-n} (m, $n = 0$–3) appeared. The intensity integration ratio was recorded again. The results are shown in Table 1.

2.4. Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me(L)$, $L = PPh_3,\ PPh_2Py,\ PPhPy_2,\ PPy_3$

$(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ (0.50 g, 2.5 mmol) and the ligand L (2.5 mmol) were dissolved in THF (10 mL, freshly distilled) and refluxed for 48 h. The mixture, an orange solution, was allowed to cool down to room temperature

Table 1
The measured equilibrium constants of $[FpP1]^+ + P2 \rightarrow P1 + [FpP2]^+$[a]

Reactant	PPh_3	PPh_2Py	$PPhPy_2$	PPy_3	
$FpPPh_3^+$	1	4.76[b]	10.7	18.7	PPh_3
	1	5.41[c]	11.4	25.6	
	1	5.05[d]	11.2	20.4	
	1	4.36[e]	10.7	16.7	
	$K_{11} = 1$	$K_{12} = 4.90(44)$[f]	$K_{13} = 11.0(4)$	$K_{14} = 20.3(38)$	
$FpPPh_2Py^+$	0.210	1	2.25	3.93	PPh_2Py
	0.185	1	2.11	4.74	
	0.198	1	2.22	4.03	
	0.229	1	2.45	3.69	
	$K_{21} = 0.205(19)$	$K_{22} = 1$	$K_{23} = 2.25(14)$	$K_{24} = 4.10(45)$	
$FpPPhPy_2^+$	0.0932	0.444	1	1.74	$PPhPy_2$
	0.0876	0.474	1	2.24	
	0.0893	0.450	1	1.82	
	0.0938	0.408	1	1.51	
	$K_{31} = 0.0910(30)$	$K_{32} = 0.444(27)$	$K_{33} = 1$	$K_{34} = 1.83(31)$	
$FpPPy_3^+$	0.0535	0.254	0.575	1	PPy_3
	0.0390	0.211	0.446	1	
	0.0491	0.248	0.549	1	
	0.0599	0.271	0.662	1	
	$K_{14} = 0.0504(88)$	$K_{42} = 0.246(25)$	$K_{43} = 0.558(89)$	$K_{44} = 1$	
	$FpPPh_3^+$	$FpPPh_2Py^+$		$FpPPhPy_2^+$	$FpPPy_3^+$ Product

[a] $Fp = (\eta^5\text{-}C_5H_5)Fe(CO)_2$, P1, P2 = PPh_3, PPh_2Py, $PPhPy_2$, PPy_3.
[b] With the initial condition: $3FpPPh_3^+PF_6^- + PPh_2Py + PPhPy_2 + PPy_3$.
[c] With the initial condition: $3FpPPh_2Py^+PF_6^- + PPh_3 + PPhPy_2 + PPy_3$.
[d] With the initial condition: $3FpPPhPy_2^+PF_6^- + PPh_3 + PPh_2Py + PPy_3$.
[e] With the initial condition: $3FpPPy_3^+PF_6^- + PPh_3 + PPh_2Py + PPhPy_2$.
[f] Average (standard deviation) of experiments b–e.

then the insoluble solid was removed by passing through a pad of celite. The solvent was removed under vacuum. The residue was dissolved in minimal CH_2Cl_2, mixed well with a small quantity of alumina and packed on the top of an alumina column. The bands were eluted first with 1:10 EtOAc/hexane to remove the trace amount of yellow $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$. The acetyl complexes $(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me(L)$ were collected using eluents of higher polarity: with 1:5 EtOAc/hexane for L = PPh_3; with 1:2 EtOAc/hexane for L = PPh_2Py; with 3:1 EtOAc/hexane for L = $PPhPy_2$; and with 3.5:1 EtOAc/hexane for L = PPy_3.

$(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me(PPh_3)$: yield 0.59 g (59%); IR (CH_2Cl_2): ν_{CO} 1916 (s) 1601 (m) cm^{-1}; ^{31}P NMR ($CDCl_3$): δ 75.23 (s); Literature [27] IR ($CHCl_3$): ν_{CO} 1920 (vs, br), 1598 (s) cm^{-1}.

$(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me(PPh_2Py)$: yield 0.53 g (47%); mp: 132–133 °C; IR (CH_2Cl_2): ν_{CO} 1921 (s), 1599 (m) cm^{-1}; ^{31}P NMR ($CDCl_3$): δ 80.9 (s); ^1H NMR ($CDCl_3$): δ 8.68 (d, $^4J_{PH} = 3.94$ Hz, 1H, Py), 7.18–7.60 (m, 13H, Ph and Py), 4.44 (s, 5H Cp), 2.38(s, 3H, Me); ^{13}C NMR ($CDCl_3$): δ 276.83 (b, C(O)Me), 220.07 (b, CO), 123.13–161.14 (m, Ph and Py), 84.96 (s, Cp), 52.18 (s, Me); MS (*m*/*z*): 466 (M^++1). *Anal*. Calc. for $C_{25}H_{22}NO_2FeP$: C, 65.93; H, 4.84; N, 3.08. Found: C, 65.83; H, 4.94; N, 2.87%.

$(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me(PPhPy_2)$: yield 0.55 g (48%); mp: 136–137 °C; IR (CH_2Cl_2): ν_{CO} 1923 (s), 1598 (m) cm^{-1}; ^{31}P NMR ($CDCl_3$): δ 84.6 (s); ^1H NMR ($CDCl_3$): δ 8.66 (b, 2H, Py), 7.20–7.62 (m, 12H, Ph and Py), 4.48 (s, 5H, Cp), 2.41 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): δ 276.01 (d, $^3J_{PC} = 22$ Hz, C(O)Me), 219.92 (d, $^3J_{PC} = 30$ Hz, CO), 123.14–161.00 (m, Ph and Py), 84.34 (s, Cp), 51.90 (s, Me); MS (*m*/*z*): 457 (M^++1); *Anal*. Calc. for $C_{24}H_{21}N_2PFeO_2$: C, 63.16; H, 4.61; N, 6.14. Found: C, 63.51; H, 4.70; N, 5.99%.

$(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me(PPy_3)$: yield 0.58 g (51%); mp: 127–128 °C; IR (CH_2Cl_2): ν_{CO} 1927 (s) 1597 (m) cm^{-1}; ^{31}P NMR ($CDCl_3$): δ 89.7 (s); ^1H NMR ($CDCl_3$): δ 8.64 (b, 3H, Py), 7.84 (b, 3H, Py), 7.66 (b, 3H, Py), 7.22 (b, 3H, Py), 4.51 (s, 5H, Cp), 2.43 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): δ 275.93 (d, $^3J_{PC} = 23$ Hz, C(O)Me), 219.70 (d, $^3J_{PC} = 30$ Hz, CO), 122.76–161.81 (m, Ph and Py), 84.62 (s, Cp), 51.81 (d, Me, $^3J_{PC} = 4$ Hz); MS (*m*/*z*): 458 (M^++1); *Anal*. Calc. for $C_{23}H_{20}N_3PFeO_2$: C, 60.39; H, 4.38; N, 9.19. Found: C, 60.23, H4.41; N, 9.36%.

2.5. Cyclic voltammetry study

The cyclic voltammograms of 10^{-3} M $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L^+][PF_6^-]$ and $(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me(L)$ where L = PPh_3, PPh_2Py, $PPhPy_2$, and PPy_3 were measured at room temperature on 10^{-1} M $[Bu_4N^+][PF_6^-]$ in CH_2Cl_2 solution. The working electrode was a glassy cabon electrode. The reference electrode was $Ag/AgNO_3$ for use in non-aqueous systems. The scan rate was 100 mV/s in the range of −1500 to 0 mV for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L^+]$

complexes and in the range of −500 to +500 mV/s for acetyl complexes, potentials being relative to ferrocene$^{0,+}$ (0.281 V). For acetyl complexes with the phosphines bearing at least one Py group, only oxidative waves were recorded, no corresponding reductive peaks being observed. For $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L^+]$ complexes, only reductive and no oxidative waves were observed. The following is the listing of measured potentials:

Complex	Potential (V)
$(\eta^5\text{-}C_5H_5)_2Fe^{0,+}$	0.281
$(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me(PPh_3)^{0,+}$	0.244
$(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me(PPh_2Py)^{0,+}$	0.227[a]
$(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me(PPhPy_2)^{0,+}$	0.200[a]
$(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me(PPy_3)^{0,+}$	0.195[a]
$(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3{}^{+,0}$	−1.234[b]
$(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_2Py^{+,0}$	−1.353[b]
$(\eta^5\text{-}C_5H_5)Fe(CO)_2PPhPy_2{}^{+,0}$	−1.380[b]
$(\eta^5\text{-}C_5H_5)Fe(CO)_2PPy_3{}^{+,0}$	−1.414[b]

[a] Only oxidative wave observed.
[b] Only reductive wave observed.

3. Results and discussion

The preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)C(O)MePPh_nPy_{3-n}$ complexes proceeded smoothly, following the literature procedure of $(\eta^5\text{-}C_5H_5)Fe(CO)C(O)MePPh_3$ [27] and gave 47–59% isolated yields. The PPh_nPy_{3-n} analogs were characterized with mp, IR, NMR, MS, and elemental analysis, where the spectroscopic data are reasonable. The ν_{CO} stretching frequencies of the acetyl complexes increase in the following order, e.g., 1916 cm^{-1} for the PPh_3 complex, 1921 cm^{-1} for the PPh_2Py complex, 1923 cm^{-1} for the $PPhPy_2$ complex, and 1927 cm^{-1} for the PPy_3 complex. Clearly there is a decrease in backbonding from Fe to the CO ligand with an increase of Py-groups, suggesting that PPy_3 is the least donating arylpyridylphosphine in the series. On the other hand, the CV oxidative wave of the acetyl complex shows a decrease in potential (0.244 V, 0.227_{irrev} V, 0.200_{irrev} V, and 0.195_{rrev} V corresponding to 0, 1, 2, and 3 Py groups), indicative of PPy_3 the best donating ligand in the series, making $(\eta^5\text{-}C_5H_5)Fe(CO)C(O)MePPy_3$, the easiest to be oxidized. The ν_{CO} stretching frequencies and E° values are in opposite directions! The pK value of $HPPh_nPy_{3-n}{}^+$ is not a good indicator here because of pyridyl-N complication to the P base site – the titration curves of PPh_nPy_{3-n} ($n = 1$–3) using an acid are hardly resolved. It is not conclusive, based on one of the Giering's parameters, to specify the best donor ligand in the PPh_nPy_{3-n} series.

The preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_nPy_{3-n}{}^+][PF_6{}^+]$ follows the ETC PPh_nPy_{3-n} ligand replacement for I^- on $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$. The yields are excellent (in 77–90% isolated yields) and the spectroscopic data are in agreement with the structural formula.

The ^{31}P resonances of free PPh_nPy_{3-n} ligands are seen to be more downfield with more Py groups (δ −4.7, −3.2, −1.9, and −0.6 for 0, 1, 2 and 3 Py-groups, respectively). Given a Ph-group contribution as σ_{Ph} and Py-group contribution as σ_{Py}, the relationship between the chemical shifts and the group contributions is linear, namely,

$$\delta(\text{free ligand}) = -4.65\delta + \sum_i \sigma_i$$

where σ_i is σ_{Ph} (=0.00δ) and σ_{py} (=1.36δ). Upon complexation, the ^{31}P resonances of the acetyl complexes $(\eta^5\text{-}C_5H_5)Fe(CO)C(O)MePPh_nPy_{3-n}$ are δ 75.2, 80.9, 84.6, and 89.7, respectively, in the order of increasing number of Py-groups. The complexation shifts Δ (=δ of complex − δ of ligand) are 79.9–90.3 δ downfield. Employing the same group contribution σ_i as for the free ligands, the ^{31}P chemical shifts of the acetyl complexes could be calculated within ±0.7 δ, in the linear fitting as follows:

$$\delta_{(\text{acetyl complex})} = 75.52\delta + 3.47\left(\sum_i \sigma_i\right)$$

where a ratio of 3.47 is necessary. Greater than 1.00, this constant suggests an amplification about the phosphine group contributions upon complexation. The similar analysis, when applied to the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_nPy_{3-n}{}^+]$ series, results in complexation shifts Δ ranging from 67.2 to 76.6 δ downfield, and a linear fitting of

$$\delta_{(\text{cation complex})} = 64.13\delta + 3.25\left(\sum_i \sigma_i\right).$$

The calculated chemical shifts and the observed ones are within ±2.0 δ. The ratio 3.25 is also suggestive of an amplification. Upon complexation, the PPh_nPy_{3-n} series is apparently different from the PPh_nMe_{3-n} series because in the latter case, the linear regression for ligands PPh_nMe_{3-n} and the corresponding complexes $(\eta^4\text{-}exo\text{-}MeC_5H_5)Fe(CO)_2PPh_nMe_{3-n}$ indicates a regulation, instead of an amplification, about the phosphine group contributions upon complexation where the ratio is only 0.85 that is less than 1.00 [28].

The ν_{CO} stretching frequencies of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_nPy_{3-n}{}^+]$ series are not very much different and are not conclusive in differentiating the PPh_nPy_{3-n} donor capability at all. Similar to the reported CV of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3{}^+]$ by Stweigart et al. [18], the cyclic voltammograms of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_nPy_{3-n}{}^+]$ in our study gave irreversible, reductive waves (−1.234 V, −1.353 V, −1.380 V, −1.414 V, in the order of 0, 1, 2, and 3 Py groups), indicative of a reactivity after being reduced. It is then worth trying the phosphine-exchange experiments. A 10 mm coaxial NMR tube has been employed that has an inner-tube containing $PPh_3(O)/CDCl_3$ and the outer-tube containing a CH_3CN solution of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$-complex and phosphines. For example, the ^{31}P NMR spectrum for a 3:1:1:1 mixture of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3{}^+]$/$PPy_3$/$PPhPy_2$/$PPh_2Py$ gave respective peaks at δ 62.5,

−0.6, −1.9, −3.2 and intensity integration ratios of ca. 19:6:6:6. After the addition of trace amount of $(\eta^5\text{-}C_5H_5)_2Co$, an initiator to activate the 17e–19e pathway, the mixture reveals a ^{31}P NMR spectrum of $FpPPy_3^+$, $FpPPhPy_2^+$, $FpPPh_2Py^+$, $FpPPh_3^+$, PPy_3, $PPhPy_2$, PPh_2Py, PPh_3 with respective peaks at δ 76.1, 74.0, 70.5, 62.5, −0.6, −1.9, −3.2, −4.7 and intensity integration ratios of ca. 10.80:10.47:8.08:7.94:2.36:3.99:6.94:32.46, respectively. The change of the spectrum is both instantaneous and extensive. The time delay between two spectra is less than a few minutes, barely enough for one to introduce the $(\eta^5\text{-}C_5H_5)_2Co$ reductant to the 10 mm NMR tube and set up a new NMR experiment. Four new species are formed after addition of $(\eta^5\text{-}C_5H_5)_2Co$ – the peak at δ −4.7 is indicative of released PPh_3 and the three new resonances at δ 76.1, 74.0, and 70.5 gave evidence of the formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPy_3^+]$, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPhPy_2^+]$, and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_2Py^+]$, respectively. The intensity integration ratios for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPy_3^+]$, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPhPy_2^+]$, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_2Py^+]$, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+]$, PPy_3, $PhPy_2$, PPh_2Py, and PPh_3 (in decreasing order of δ values) become ca. 11:10:8:8:2:4:7:32. The ratios stay the same after 24 h, i.e., the phosphine exchange reaction with a radical process proceeds to a completion in a time scale of sub-minutes.

For a relevant pair of phosphines, the equilibrium constant K of Eq. (1) could be calculated based on the intensity integration ratio. Thus, out of 4 complexes and 4 ligands involved after the addition of $(\eta^5\text{-}C_5H_5)_2Co$, there are 16 phosphine exchange equilibrium constants K_{ij} ($i, j = 1$–4), defined in Table 1, among which four are the self-exchange ($K_{11} = K_{22} = K_{33} = K_{44} = 1$), six the forward reactions (K_{ij} with $i < j$) and six the reverse reactions (K_{ij} with $i > j$). For instance in the equation

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+ + PPy_3 = PPh_3 + (\eta^5\text{-}C_5H_5)Fe(CO)_2PPy_3^+$$

$$K_{14} = [(\eta^5\text{-}C_5H_5)Fe(CO)_2PPy_3^+][PPh_3] / [(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+][PPy_3] \equiv (11)(32)/(8)(2) = 22.$$

Listed in Table 1, the actual calculations have been performed using the intensity integration values in two decimal points (K_{14} is 18.7, instead of the approximate 22). The rest of equilibrium constants are also calculated in this manner. The conversion factors relating the concentration of a PPh_nPy_{3-n} or a $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_nPy_{3-n}^+]$ and the intensity integration in ^{31}P NMR spectrum may be different. In our experience, these factors are about the same if an error of ±10% is taken into consideration. Experiments with simultaneously present arylpyridylphosphines indeed deliver a very nice internal consistency. The initial concentrations with three portions of one $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ phosphine complex and one portion each of the remaining arylpyridylphosphines are listed in Table 1 that summarizes the phosphine exchange results.

3.1. Fp^+-affinity for PPh_nPy_{3-n}

The equilibrium constants in Table 1 clearly reveal that for the series of arylpyridylphosphines PPh_nPy_{3-n}, the donor capability increases in the order $PPh_3 < PPh_2Py < PPhPy_2 < PPy_3$. The standard deviations of K_{ij}'s are within 20% which seems reasonable in view of uncorrected instrumentation factors. These equilibrium constants could further be deducted into a much more easily understood Fp^+-affinity scale where $Fp^+ = (\eta^5\text{-}C_5H_5)Fe(CO)_2^+$, which is a measure of the association between a PPh_nPy_{3-n} ligand and the Fp^+ cation:

$$Fp^+ + PPh_3 = FpPPh_3^+ \quad K_1 = [FpPPh_3^+]/[Fp^+][PPh_3]$$
$$Fp^+ + PPh_2Py = FpPPh_2Py^+ \quad K_2 = [FpPPh_2Py^+]/[Fp^+][PPh_2Py]$$
$$Fp^+ + PPhPy_2 = FpPPhPy_2^+ \quad K_3 = [FpPPhPy_2^+]/[Fp^+][PPhPy_2]$$
$$Fp^+ + PPy_3 = FpPPy_3^+ \quad K_4 = [FpPPy_3^+]/[Fp^+][PPy_3]$$

Hence, the K_{ij}'s listed in Table 1 could be factored, i.e., $K_{12} = K_2/K_1$, $K_{13} = K_3/K_1$, etc. As Fp^+ is only loosely defined and PPh_3 is the most used triarylphosphine, K_1 could reasonably assume to be unitary in this Fp^+-affinity scale to quantify the parameter. Then $K_2 = 4.90$, $K_3 = 11.0$, and $K_4 = 20.3$.

The incoming phosphine replacement for CO is generally more difficult than the replacement for phosphine in view of a stronger Fe–C(CO) bond than Fe–P. In the present radical phosphine exchange reactions, the substitution by excess PPh_nPy_{3-n} for CO was not observed. We believe that the large cone angles of PPh_nPy_{3-n} are important here because in the 17e–19e pathways, the reaction rate is very sensitive to steric hindrance. For phosphines of smaller cone angles, e.g., PPh_2Me ($\Theta = 136°$), we have observed that the phosphine exchange experiment starting PPh_2Me and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3^+]$ as initialized with a catalytic amount of $(\eta^5\text{-}C_5H_5)_2Co$, yielded both $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_2Me^+]$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_2Me)_2^+]$ as products [29]. The double replacement product could be reduced at lower temperatures. A study is now underway in a hope to extend the Fp^+-affinity scale to PPh_2Me and/or phosphines of smaller cone angles.

4. Conclusion

Application of a radical process results in the rapid phosphine exchange between the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PAr_3^+]$ complexes and the PR_3 ligands (PAr_3, $PR_3 = PPh_nPy_{3-n}$, $n = 0$–3) where the donor capability increases in the order $PPh_3 < PPh_2Py < PPhPy_2 < PPy_3$ with quantified Fp^+ affinity scales at 1, 4.90, 11.0, and 20.3, respectively.

Acknowledgements

Thanks are due to the National Science Council and Academia Sinica for the kind financial support.

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