Application of electron-transfer chain catalysis: preparation of bridged $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\mu\text{-diphosphine})^{2+}]$ complexes without chelated $[(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^2\text{-diphosphine})^+]$ byproducts

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This article is dedicated to the memory of the late Professor John A. Osborn.

Abstract – The ligand substitution by diphosphine L–L on $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ usually results in the chelated $[(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^2\text{-L–L})^+][I^-]$ product exclusively. One could suppress the chelated complexes and selectively prepare the bridged $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\mu\text{-L–L})^{2+}]$ complexes by application of the electron-transfer chain catalysis with a chemical initiation. Introducing a catalytic amount of reductant at low temperature to the mixture of 2:1 $(\eta^5\text{-}C_5H_5)Fe(CO)_2I/L\text{–L}$ in THF selectively produces the bridged complexes in 78–93% isolated yields where L–L is $Ph_2P(CH_2)_nPPh_2$, $n = 1\text{–}4$, or $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$. *To cite this article: J. Peng, L.-K. Liu, C. R. Chimie 5 (2002) 319–324* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

electron-transfer chain catalysis / ligand substitution reaction / bridged complexes

Résumé – La substitution de ligand induite par une diphosphine L–L sur le complexe $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ conduit généralement exclusivement au produit chélaté $[(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^2\text{-L–L})^+][I^-]$. Il s'est avéré possible d'éviter les complexes chélatés et de préparer sélectivement les complexes pontés $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\mu\text{-L–L})^{2+}]$ en appliquant une catalyse en chaîne par transfert d'électron, avec initiation chimique. L'introduction à basse température d'une quantité catalytique de réducteur aux mélanges 2:1 $(\eta^5\text{-}C_5H_5)Fe(CO)_2I/L\text{–L}$ dans le THF produit sélectivement les complexes pontés, avec des rendements en produit isolé de 78–93 %, avec L–L = $Ph_2P(CH_2)_nPPh_2$ ($n = 1\text{–}4$) ou $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$. *Pour citer cet article : J. Peng, L.-K. Liu, C. R. Chimie 5 (2002) 319–324* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

catalyse en chaîne par transfert d'électron / reaction de substitution de ligand / complexes pontés

1. Introduction

The ligand substitution reaction on $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ (X = halides) with a monophosphine ligand L yields $(\eta^5\text{-}C_5H_5)Fe(CO)(L)X$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(L)^+][X^-]$ [1, 2]. Multiple substitution, e.g., $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)_2^+][X^-]$, could be obtained with excess L and under forcing conditions [3–5]. Similar reaction when extended to diphosphine L–L, gives $[(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^2\text{-L–L})^+][X^-]$ almost exclusively because of the well-known chelate effect. Chelated $[(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^2\text{-dppe})^+]$ complex (dppe = $Ph_2PCH_2CH_2PPh_2$) with various counter anions has been reported [6–14]. Coville et al. established the facile synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^2\text{-dppe})^+]$ from $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and dppe, without observing the bridged $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\mu\text{-dppe})^{2+}]$ complex [13].

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Demonstrated here, we have applied the 17e–19e reaction pathway to the substitution reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (2 mol) and L–L (1 mol) and prepared the bridged $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\mu\text{-L-L})^{2+}]$ complexes selectively, where L–L is $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, dppm; $n = 2$, dppe; $n = 3$, dppp; $n = 4$, dppb) or $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$ (dppf). The reaction of phosphine replacing iodide on $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ has a smaller barrier than replacing CO ligand on $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(L)^+]$ if the activation energies are approximately the Fe–I and Fe–CO bond energies, respectively. Reportedly Fe–I bond energy is 177 kJ mol^{-1} [15] and Fe–CO bond energy 217 kJ mol^{-1}, the latter taking into consideration the energy required to promote the metal atom from high spin electronic state to the low spin valence configuration [16]. On top of this intuition, we have worked on the kinetics of 'electron catalysis' reductively in 2:1 $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$/L–L systems and found that the high-energy, electron-transfer chain processes (ETC [17–23], vide infra) indeed suppressed the formation of chelated $[(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^2\text{-L-L})^+]$ complexes.

2. Experimental section

2.1. General

All manipulations were performed under an atmosphere of pre-purified nitrogen with standard Schlenk techniques, and all solvents distilled from an appropriate drying agent [24]. IR spectra were recorded in CH$_3$CN or CH$_2$Cl$_2$, using CaF$_2$ optics on a Perkin-Elmer 882 spectrophotometer. The ^{1}H NMR and ^{31}P NMR spectra were obtained on Bruker AC200/AC300 spectrometers, with ^{1}H chemical shifts reported in δ values, downfield positive, relative to the residual solvent resonance of CDCl$_3$ (δ 7.24) or CD$_3$CN (δ 1.93) and ^{31}P chemical shifts, using 85% H$_3$PO$_4$ as an external standard (δ 0.00). Micro-analytical data were obtained with the use of a Perkin-Elmer 240C elemental analyzer independently operated by the Institute of Chemistry, Academia Sinica. All reagents were obtained from commercial sources and used without further purification. $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ was prepared according to a literature procedure [25, 26].

2.2. Preparative method

The following is a general reaction of 2:1 $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and L–L after chemical initiation. $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (638 mg, 2.1 mmol) and L–L (1.0 mmol; dppe 398 mg; dppp 412 mg; dppb 426 mg; dppf 560 mg) were dissolved in THF (20 ml) and maintained at –78 °C. Addition of trace $(\eta^5\text{-}C_5H_5)_2Co$,

then removal of the cold bath to allow a slow warming of the solution to 0 °C resulted in a large quantity of yellow precipitates. At this stage, Et$_2$O-containing trace H$_2$O was added to the mixture to stop the reaction, followed by filtration and washing of the precipitates with Et$_2$O (20 ml × 3). The precipitates together with excess NH$_4$PF$_6$ were re-dissolved in CH$_3$CN and vigorously stirred before addition of sufficient H$_2$O. Filtration then washing the precipitates with H$_2$O (20 ml × 3) and Et$_2$O (20 ml × 3) produced the respective bridged products.

$[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\mu\text{-dppe})^{2+}][PF_6^-]_2$ (**1**), yield 92% (959 mg, 0.92 mmol): IR (CH$_3$CN) ν_{CO} 2056(s), 2012(s) cm^{-1}; ^{31}P{^{1}H} NMR (CD$_3$CN) δ 62; ^{1}H NMR (CD$_3$CN) δ 7.7–7.3 (m, 20H, Ph), 5.14 (s, 10H, Cp), 2.38 (m, 4H, PPh$_2$CH_2–); ^{13}C{^{1}H} NMR (CD$_3$CN) δ 210.4 (t, J_{PC} = 12 Hz, CO), 133.6 (s, Ph), 133.1 (d, J_{PC} = 4 Hz, Ph), 130.9 (d, J_{PC} = 4 Hz, Ph) 130.2 (d, J_{PC} = 26 Hz, ipso Ph), 89.7 (s, Cp), 28.3 (t, J_{PC} = 10 Hz, PPh$_2$CH_2–).

$[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\mu\text{-dppp})^{2+}][PF_6^-]_2$ (**2**), yield 93% (982 mg, 0.93 mmol): IR (CH$_3$CN) ν_{CO} 2055(s), 2011(s) cm^{-1}; ^{31}P{^{1}H} NMR (CD$_3$CN) δ 58; ^{1}H NMR (CD$_3$CN) δ 7.6–7.3 (m, 20H, Ph), 5.13 (d, $^3J_{PH}$ = 1.4 Hz, 10H, Cp), 2.62 (m, 4H, PPh$_2$CH_2-), 1.15 (m, 2H, PPh$_2$CH$_2$CH_2-); ^{13}C{^{1}H} NMR (CD$_3$CN) δ 210.1 (d, J_{PC} = 36 Hz, CO), 133.1 (s, Ph), 132.8 (d, J_{PC} = 10 Hz, Ph), 131.1 (d, J_{PC} = 50.6 Hz, ipso Ph) 130.5 (d, J_{PC} = 11 Hz, Ph), 89.0 (s, Cp), 32.9 (dd, J_{PC} = 30 Hz, J_{PC} = 14 Hz, PPh$_2$CH_2–), 20.6 (s, PPh$_2$CH$_2$CH_2–). Anal. calcd for C$_{41}$H$_{36}$F$_{12}$Fe$_2$O$_4$P$_4$: C, 46.62; H, 3.44. Found: C, 46.36; H, 3.39.

$[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\mu\text{-dppb})^{2+}][PF_6^-]_2$ (**3**), yield 92% (991mg, 0.92 mmol): IR (CH$_3$CN) ν_{CO} 2054(s), 2011(s) cm^{-1}; ^{31}P{^{1}H} NMR (CD$_3$CN) δ 58.3; ^{1}H NMR (CD$_3$CN) δ 7.6–7.4 (m, 20H, Ph), 5.18 (d, $^3J_{PH}$ = 1.4 Hz, 10H, Cp), 2.52 (m, 4H, PPh$_2$CH_2–), 1.36 (m, 4H, PPh$_2$CH$_2$CH_2–) ; ^{13}C{^{1}H} NMR (CD$_3$CN) δ 210.8 (d, J_{PC} = 24 Hz, CO), 133.1 (s, Ph), 132.9 (s, Ph), 132.1 (d, J_{PC} = 50.4 Hz, ipso Ph), 130.5 (d, J_{PC} = 11 Hz, Ph), 89.4 (s, Cp), 32.4 (d, J_{PC} = 30 Hz, PPh$_2$CH_2-), 25.8 (d, J_{PC} = 15 Hz, PPh$_2$CH$_2$CH_2–). Anal. calcd for C$_{42}$H$_{38}$F$_{12}$Fe$_2$O$_4$P$_4$: C, 47.13; H, 3.58. Found: C, 46.97; H, 3.47.

$[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\mu\text{-dppf})^{2+}][PF_6^-]_2$ (**4**), yield, 80% (958 mg, 0.8 mmol): IR (CH$_3$CN) ν_{CO} 2055(s), 2012(s) cm^{-1}; ^{31}P{^{1}H} NMR (CD$_3$CN) δ 59; ^{1}H NMR (CDCl$_3$) δ 7.7–7.3 (m, 20H, Ph), 5.12 (d, $^3J_{PH}$ = 1.7 Hz, 10H, Cp), 4.3 (m, 2H, Cp of Fc), 3.97 (m, 2H, Cp of Fc); ^{13}C{^{1}H} NMR (CD$_3$CN) δ 210.5 (d, J_{PC} = 24 Hz, CO), 134.0 (d, J_{PC} = 55.3Hz, ipso Ph), 133.3 (s, Ph), 133.1 (s, Ph), 130.2 (d, J_{PC} = 11 Hz, Ph), 89.8 (s, Cp), 79.9 (d, J_{PC} = 7 Hz, ipso Cp of Fc), 75.8 (d, J_{PC} = 8 Hz, Cp of Fc), 75.5

(d, $J_{PC} = 11$ Hz, Cp of Fc). Anal. calcd for $C_{48}H_{38}F_{12}Fe_3O_4P_4$: C, 48.11; H, 3.20. Found: C, 47.92; H, 3.11.

2.3. Preparation of [{(η^5-C$_5$H$_5$)Fe(CO)$_2$}$_2$(μ-dppm)$^{2+}$][PF$_6^-$]$_2$

Under N$_2$ atmosphere, dppm (380 mg, 1.1 mmol) was dissolved in THF (30 ml) and kept being stirred at 0 °C. To this solution was slowly added n-BuLi (0.7 ml 1.6 M in hexane, 1.1 mmol). The solution was then allowed to return to room temperature and kept under stirring for 1 h. This mixture was added dropwise into a round-bottomed flask containing (η^5-C$_5$H$_5$)Fe(CO)$_2$I (630 mg, 2.1 mmol) in THF (20 ml) at 0 °C. The cold bath was taken away to allow the temperature of the mixture to rise to room temperature. Red colored precipitates formed. The reaction mixture was further stirred for 3 h before standing still for cannula-removal of organic solvents. The precipitates were then washed with Et$_2$O (20 ml × 3) and vacuum-dried to give powders of LiI and an intermediate salt [{(η^5-C$_5$H$_5$)Fe(CO)$_2$}$_2$(μ-Ph$_2$PCHPPh$_2$)$^+$][I$^-$] (**5**) that is red in color. A CH$_3$CN solution (30 ml) containing HPF$_6$ or CF$_3$COOH (0.2 ml) and NH$_4$PF$_6$ (1.0 g) was then introduced. The color changed from red to yellow. After complete dissolution, a large quantity of H$_2$O was added to the solution to yield yellow precipitates, which were filtered and washed with H$_2$O (20 ml × 3) and Et$_2$O (20 ml × 3) to give [{(η^5-C$_5$H$_5$)Fe(CO)$_2$}$_2$(μ-dppm)$^{2+}$][PF$_6^-$]$_2$ (**6**). The intermediate salt could be purified further by passing its CH$_2$Cl$_2$ solution through a short column to remove LiI, followed by addition of hexane in order to obtain a red powder, which is moderately sensitive to oxygen and moisture.

5, Yield 82% (708 mg, 0.82 mmol): IR (CH$_2$Cl$_2$) ν_{CO} 2041(s), 1996(s) cm^{-1}; ^{31}P{^{1}H} NMR (CDCl$_3$) δ 38.9; ^{1}H NMR (CDCl$_3$) δ 7.4–7.0 (m, 20H, Ph), 4.87 (s, 10H, Cp), 1.27 (t, $^2J_{PH} = 11$ Hz, 1H, PPh$_2$CHPPh$_2$). Anal. calcd for $C_{39}H_{31}Fe_2O_4P_2I$: C, 54.20; H, 3.62. Found: C, 53.89; H, 3.60.

6, Yield 78% (802 mg, 0.78 mmol): IR (CH$_3$CN) ν_{CO} 2059(s), 2017(s) cm^{-1}; ^{31}P{^{1}H} NMR (CD$_3$CN) δ 63; ^{1}H NMR (CD$_3$CN) δ 7.5–7.3 (m, 20H, Ph), 5.0 (s, 10H, Cp), 3.63 (t, $^2J_{PH} = 7$ Hz, 2H, PPh$_2$CH_2PPh$_2$); ^{13}C{^{1}H} NMR (CD$_3$CN) δ 210.2 (t, $J_{PC} = 11$Hz, CO), 133.5 (s, Ph), 132.8 (s, Ph), 130.4 (s, Ph) 128.6 (t, $J_{PC} = 13$ Hz, $ipso$ Ph), 89.8 (s, Cp), 34.4 (t, $J_{PC} = 8.5$ Hz, PPh$_2$CH_2PPh$_2$). Anal. calcd for $C_{39}H_{32}F_{12}Fe_2O_4P_4$: C, 45.56; H, 3.14. Found: C, 45.58; H, 3.16.

2.4. X-ray structure analysis

Crystals of **4** suitable for X-ray diffraction analysis were grown from CH$_3$CN/Et$_2$O by a slow evaporation method. Diffraction intensities were measured with background counts made for half the total scan time on each side of peak. Three standard reflections, re-measured after every hour, showed no significant decrease in intensity during data collection. Data were corrected for Lorentz polarization and absorption (empirical Φ corrections). The structure was solved by direct methods MULTAN [27]. Calculations and full matrix least-squares refinements were performed utilizing the NRCVAX program package [28]. All non-H atoms were refined with anisotropic thermal parameters with all hydrogen atoms fixed (C–H = 1.00 Å) at an anisotropic convergence stage. Scattering factor curves of Fe, P, F, O, C, and H were taken from the International Tables [29]. A molecular plot is given in Fig. 1.

Crystal data of **4**: $C_{48}H_{38}F_{12}Fe_3O_4P_4$, $Fw = 1198.24$, Monoclinic $P2_1/n$, $a = 10.698(1)$ Å, $b = 17.752(2)$ Å, $c = 12.458(1)$ Å, $\beta = 96.78(1)°$, $V = 2349.4(5)$ Å, $Z = 2$, $F(000) = 1207.83$, $D_{calc} = 1.694$ g cm^{-1}, $T = 298$ K, $\mu = 1.14$ cm^{-1}, $\lambda = 0.710\,70$ Å, Nonius CAD-4 diffractometer, $-12 < h < 12$, $0 < k < 21$, $0 < l < 14$, 4130 unique reflections, 3096 observations [$I_0 > 2.5\,\sigma(I_0)$], transmission factors 0.949–0.999, 55 atoms, 322 parameters, $R = 0.036$, $R_W = 0.041$, GOF = 1.54.

3. Results and discussion

3.1. Preparations in the literature

There are three reported procedures concerning the preparation of bridged [{(η^5-C$_5$H$_5$)Fe(CO)$_2$}$_2$(μ-dppe)$^{2+}$] complexes. Meyer et al. reacted [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_2$ and Fe(ClO$_4$)$_3$ in acetone to produce [(η^5-C$_5$H$_5$)Fe(CO)$_2$(acetone)$^+$] first, which was then added to only 1/8 equiv of dppe in C$_6$H$_6$ to result in [{(η^5-C$_5$H$_5$)Fe(CO)$_2$}$_2$(μ-dppe)$^{2+}$][ClO$_4^-$]$_2$ [30]. Similarly, upon treatment of 1/9 equiv of dppm, [(η^5-C$_5$H$_5$)Fe(CO)$_2$(acetone)$^+$] yielded bridged [{(η^5-C$_5$H$_5$)Fe(CO)$_2$}(μ-dppm)$^{2+}$][ClO$_4^-$]$_2$. The method of Meyer is strictly 16e–18e, the labile acetone being replaced by phosphine with [(η^5-C$_5$H$_5$)Fe(CO)$_2$(acetone)$^+$] in large excess. Haines et al. reported that treatment of 2 equiv of (η^5-C$_5$H$_5$)Fe(CO)$_2$Cl with 1 equiv of dppe in C$_6$H$_6$ for 15 h at room temperature effected the displacement of chloride and afforded a yellow crystalline derivative characterized as bridged [{(η^5-C$_5$H$_5$)Fe(CO)$_2$}$_2$(μ-dppe)$^{2+}$][Cl$^-$]$_2$ [6]. Sellmann et al. reported in 1977 and 1986 that the reaction of equimolar (η^5-C$_5$H$_5$)Fe(CO)$_2$Cl and dppe in a small volume of THF produced, after anion exchange, both bridged [{(η^5-C$_5$H$_5$)Fe(CO)$_2$}$_2$(μ-dppe)$^{2+}$][PF$_6^-$]$_2$ and chelated [(η^5-C$_5$H$_5$)Fe(CO)(η^2-dppe)$^+$][PF$_6^-$] in the paste [8, 31].
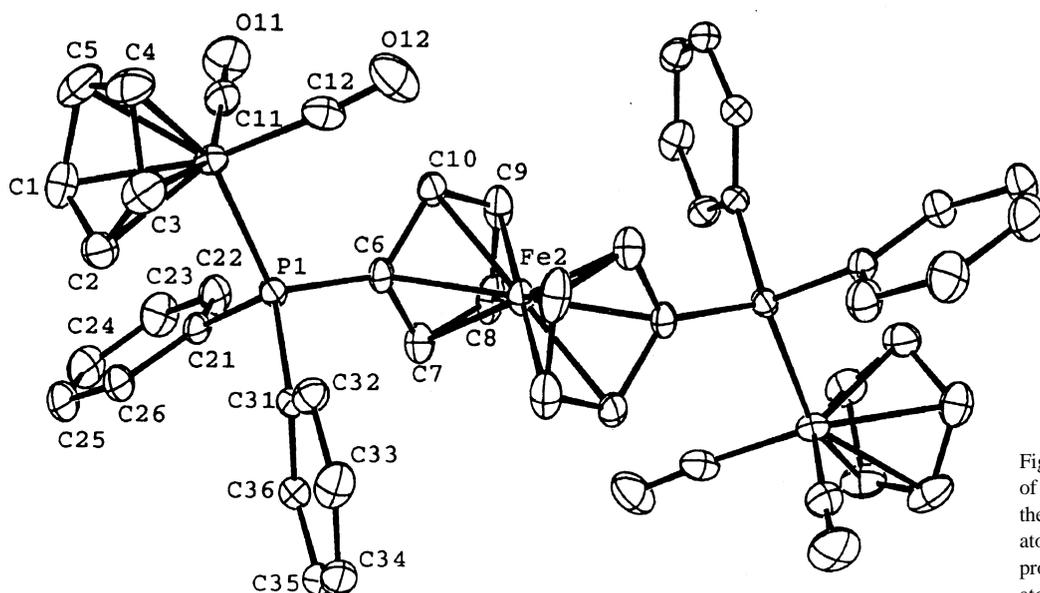
Fig. 1. ORTEP molecular plot of the dication of **4**. The thermal ellipsoids for the atoms are plotted at the 50% probability level. Hydrogen atoms are omitted for clarity.

The methods of Haines and Sellmann are likely to follow a radical pathway. In Haines' procedure, an initiation seems necessary, presumably by room light with an unknown period of induction, whereas in Sellmann's procedure, the ratio of bridged product to chelated product is quite unpredictable.

3.2. Application of ETC catalysis: preparation of 1–4

Our approach here to the preparation of **1–4**, the bridged $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\mu\text{-}L\text{-}L)^{2+}]$ complexes isolated as the $[PF_6^-]$ salts, has been an introduction of a catalytic amount of reductive initiator at low temperature to the THF mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and L–L in 2:1 molar ratio in order to get started with the ETC pathway. The isolated yields are in the range of 80–93% (Fig. 2). The reactions have been checked with ^{31}P NMR on the crude mixtures, the spectra being always suggestive of yields of more than 95% for the bridged $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\mu\text{-}L\text{-}L)^{2+}]$ complexes. The reaction time recorded in the procedure is just a few minutes. The reaction temperature is usually between low temperature and room temperature.

In our earlier experiences, the reaction of 1:1 $(\eta^5\text{-}C_5H_5)Fe(CO)_2I/PPh_3$ in THF at –78 °C, after reductive initialization with a dilute lithiated reagent or $(\eta^5\text{-}C_5H_5)_2Co$, follows the 17e–19e pathway and instantaneously gives precipitates of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)^+][I^-]$, iodide being selectively replaced by PPh_3 (Fig. 3) [32]. The ligand exchange at the 19e Fe-center is rapid, and then the immediately following cross electron-transfer propagation completes the catalytic cycle, resulting in an overall reaction without net redox change.
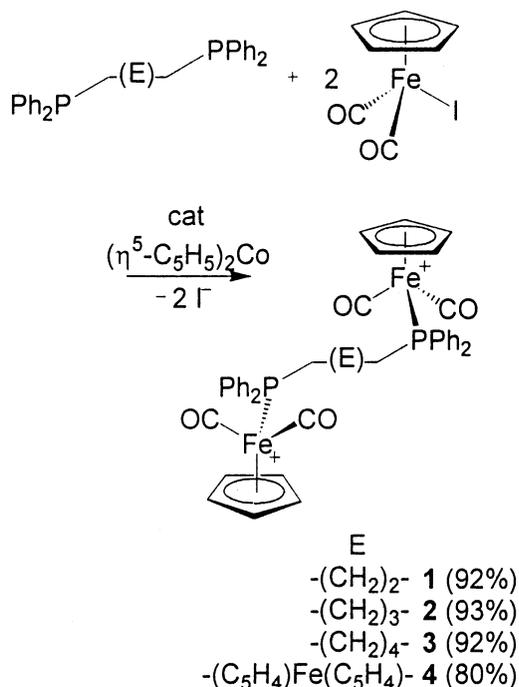

Fig. 2. Preparation of compounds **1–4**.

E
-(CH_2)_2- **1** (92%)
-(CH_2)_3- **2** (93%)
-(CH_2)_4- **3** (92%)
-(C_5H_4)Fe(C_5H_4)- **4** (80%)

The extra electron is antibonding in nature, which effectively decreases the barrier to break the Fe–I bond. At the beginning, a small amount of 18e $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ is chemically reduced by $(\eta^5\text{-}C_5H_5)_2Co$ to 19e $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I^-]$ radical anion. The 17e–19e process is initiated accordingly in a controllable manner, extending the earlier PPh_3 system [32, 33] to diphosphine systems. We have regarded each L–L as two independent phosphine ligands. We
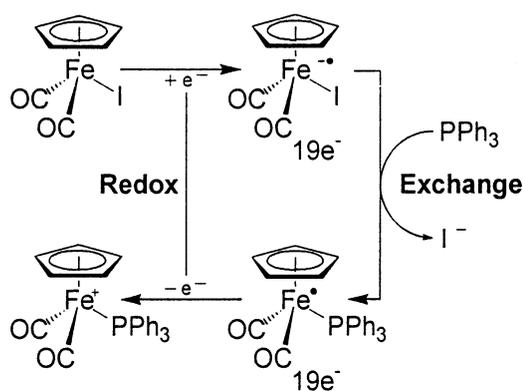
Fig. 3. Reaction of 1:1 $(\eta^5\text{-}C_5H_5)Fe(CO)_2I/PPh_3$ in THF at –78 °C, after reductive initialization with a dilute lithiated reagent or $(\eta^5\text{-}C_5H_5)_2Co$, following the 17e–19e pathway and giving instantaneously precipitates of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)^+][I^-]$, iodide being selectively replaced by PPh_3.

have also taken the advantage that iodide salts of bridged $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\mu\text{-L–L})^{2+}]$ complexes precipitate from the THF solution. The initial 2:1 molar ratio of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and L–L is kept to avoid the chelated product, which was observed in Sellmann's procedure. This improved procedure is satisfactory and essentially quantitative.

Dilute MeLi could also be used to replace $(\eta^5\text{-}C_5H_5)_2Co$ as the reductive initiator during preparation [34]. However, if more than a catalytic amount is introduced to the mixture of 2:1 $(\eta^5\text{-}C_5H_5)Fe(CO)_2I/L–L$ in THF at low temperature, $\{(\eta^4\text{-}MeC_5H_5)Fe(CO)_2\}_2(\mu\text{-L–L})$, among others, is often obtained, as derived from nucleophilic Me-addition on

the $(\eta^5\text{-}C_5H_5)$-rings of bridged $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(\mu\text{-L–L})^{2+}]$ complexes [35]. With 2 mol of MeLi introduced to the 2:1 $(\eta^5\text{-}C_5H_5)Fe(CO)_2I/L–L$ solution, $\{(\eta^4\text{-}MeC_5H_5)Fe(CO)_2\}_2(\mu\text{-L–L})$ will be isolated in 62–68% yields, because the stoichiometric amount of Me-anion adds onto the $(\eta^5\text{-}C_5H_5)$-rings nucleophically, as detailed elsewhere [35].

3.3. Preparation of 6

In structural inorganic chemistry, especially in self-assembly, metal centers often act as nodes and bidentate diphosphines as connecting units. Diphosphine ligands may bind in many different ways (chelate vs bridge, *syn* conformation vs *anti* conformation when bridging) according to the length and rigidity of spacer [36]. As there is just one methylene between two phosphines in dppm, its chemistry is different from other diphosphine ligands.

The ETC reaction between 2 mol of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and 1 mol of dppm, initiated by $(\eta^5\text{-}C_5H_5)_2Co$ or diluted lithiated reagent, gives $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-dppm})^+]$ with 1 mol of non-reacted $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$. Presumably, the monodentate $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-dppm})^+]$ is sterically too demanding to proceed with the ETC-catalyzed substitution for iodide on the second $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$. Currently, we have attempted to remove such a steric energy with the methylene in dppm and successfully employed the strategy of deprotonation–substitution–reprotonation in the preparation of **6**. The methylene of dppm is deprotonated by *n*-BuLi first. Then the resultant anionic $Ph_2PCH^-PPh_2$ solution is employed
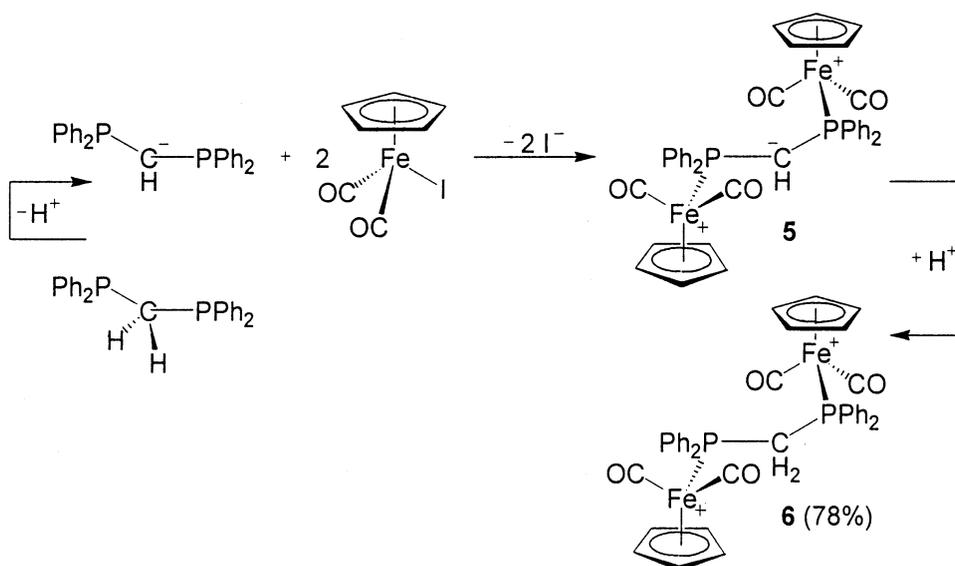

Fig. 4. Preparation of compounds **5** and **6**.

as the diphosphine and at the same time, initial drops may function as the reductive initiator in the reaction with 2 equiv of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ (Fig. 4). The substitution produces an intermediate salt **5**, which is protonated and anion-exchanged with NH_4PF_6 to yield successfully **6** in 78% isolated yield.

Electronically, it is also better along the reaction coordinate, using anionic $Ph_2PCH^-PPh_2$ to bridge two cationic Fe centers than using neutral dppm directly.

3.4. X-ray structure of 4

Single crystal X-ray diffraction of **4** was studied to support the molecular connectivity of this series as the bridged complexes. The ferrocenyl Fe-atom is on a crystallographic inversion center and the ferrocenyl $(\eta^5\text{-}C_5H_5)$-rings are staggered with each other (Fig. 1). The peripheral Fe centers are octahedral in their coordination sphere. The structural parameters are normal.

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