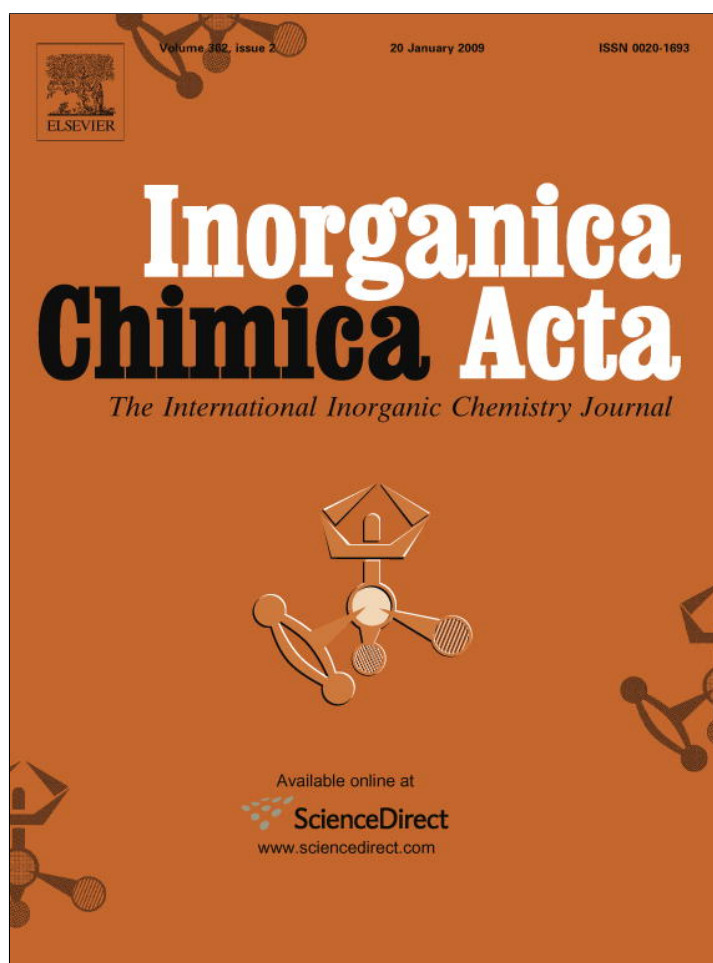




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Neighbouring metal induced oxidative addition at the iron centre amongst the iron–arylpdridylphosphine complexes

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ABSTRACT

Complexes of the type $(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{P})$ ($\text{P} = \text{PPh}_2\text{Py}$ **3**, PPhPy_2 **4**, PPy_3 **5**; $\text{Py} = 2\text{-pyridyl}$) were satisfactorily prepared. Upon treatment of **3** with $\text{M}(\text{CO})_3(\text{EtCN})_3$ ($\text{M} = \text{Mo}$, **6a**; W , **6b**), the pyridyl N-atom could be coordinated to the metal M, which then eliminates a CO ligand from the Fe-centre and induced an oxidative addition of the *endo*-C–H of $(\eta^4\text{-BuC}_5\text{H}_5)$. This results in a bridged hydrido heterodimetallic complex $[(\eta^5\text{-BuC}_5\text{H}_4)\text{Fe}(\text{CO})(\mu\text{-P,N-PPh}_2\text{Py})(\mu\text{-H})\text{M}(\text{CO})_4]$ ($\text{M} = \text{Mo}$, **7a**, 81%; W , **7b**, 76%). The reaction of **4** or **5** with **6a,b** did not give the induced oxidative addition, although these complexes contain more than one pyridyl N-atom. The reaction of **4** with $\text{M}(\text{CO})_4(\text{EtCN})_2$ ($\text{M} = \text{Mo}$, **9a**; W , **9b**) produced heterodimetallic complexes $[(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\mu\text{-P,N,N'-PPhPy}_2)\text{M}(\text{CO})_4]$ ($\text{M} = \text{Mo}$, **10a**, 81%; W , **10b**, 83%). Treatment of **5** with **6a,b** gave $[(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\mu\text{-P,N,N',N''-PPy}_3)\text{M}(\text{CO})_3]$ ($\text{M} = \text{Mo}$, **12a**, 96%; W , **12b**, 78%).

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1. Introduction

The coordination chemistry of arylpyridylphosphines $\text{PPh}_{3-n}\text{Py}_n$ ($n = 1\text{--}3$; $\text{Py} = 2\text{-pyridyl}$) has largely developed. It is of particular interest because of the use of metal complexes containing such ligands in homogeneous catalysis, especially with a potential application in aqueous media [1]. The presence of a basic N-atom in each pendant pyridine in $\text{PPh}_{3-n}\text{Py}_n$ ligands distinguishes it from PPh_3 ligand. Hence, there is enhanced acid–base chemistry involved by the presence of pyridyl N-atom(s) and more coordination modes are available for $\text{PPh}_{3-n}\text{Py}_n$ as ligand than only the P-donor mode in PPh_3 . For instance, PPh_2Py could behave in mononuclear complexes as a P-donor ligand and in dinuclear complexes as a P,N-bridging ligand with or without metal–metal bonding. PPhPy_2 and PPy_3 can bind further with a variety of coordination modes: through two pyridyl groups (N,N' ; PPh_2Py and PPy_3), through three pyridyl groups (N,N',N'' ; PPy_3), and via the phosphorus and two pyridyl groups (P,N,N' ; PPhPy_2 and PPy_3) [2].

Few years ago we reported the synthesis of $(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_{3-n}\text{Py}_n)$ ($n = 1\text{--}3$). A three-component reaction was utilized to produce the complexes. The hydride abstraction of *endo*-

hydrogen of $(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_{3-n}\text{Py}_n)$ were smoothly carried out by Lewis acid, $\text{HBF}_4 \cdot \text{OEt}_2$ to give $[(\eta^5\text{-BuC}_5\text{H}_4)\text{Fe}(\text{CO})_2(\text{PPh}_{3-n}\text{Py}_n)]^+[\text{BF}_4]^-$ ($n = 1\text{--}2$) [3].

In this paper, we incorporated the $\text{PPh}_{3-n}\text{Py}_n$ ligands into complexes of the type $(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_{3-n}\text{Py}_n)$ and studied the effect of the presence of the dangling pyridyl N-atom(s), known to be able to coordinate to a second metal centre [2]. In the case of the PPh_2Py complex which contains one pyridyl N-atom, a neighbouring Mo or W metal originally with three labile ligands could induce an oxidative addition on the Fe-centre. Similar chemistry could not be observed for the PPhPy_2 and PPy_3 analogues.

2. Experimental

2.1. General

All manipulations were performed under an atmosphere of pre-purified nitrogen with standard Schlenk techniques and a double-fold vacuum line. All solvents were distilled from an appropriate drying agent [4]. For instance, THF, Et_2O and *n*-hexane were dried over sodium benzophenone ketal. CH_3CN and $\text{CH}_3\text{CH}_2\text{CN}$ were dried over P_2O_5 and CaH_2 was used for CH_2Cl_2 . Infrared spectra were recorded in CH_2Cl_2 using CaF_2 optics on a Perkin–Elmer (FT-IR) Paragon 1000 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

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NMR δ 77.0). The ^{31}P NMR spectra were obtained on Bruker AC200/AC300 spectrometers 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 are uncorrected. Mass spectra were recorded on a VG 70 – 250S mass Spectrometer, using fast atomic bombardment technique, independently operated by the Institute of Chemistry, Academia Sinica. Chemical analysis was performed on a Perkin–Elmer 2400 CHN elemental analyzer, also independently operated by the Institute of Chemistry, Academia Sinica. Compounds **1**, [5], **2**, **3**, **4**, **5** [3], **6a,b**, [6] and **9a,b** [7] were prepared according to literature procedure. Ligands PPh_2Py [8a], PPhPy_2 [8b], PPy_3 [8c] were prepared using Li–Br exchange method in good yield. PCl_3 , PPhCl_2 , PPh_2Cl , and $o\text{-C}_5\text{H}_4\text{NBr}$ were obtained from commercial sources, distilled twice and degassed prior to use. Other reagents were obtained from commercial sources and used without further purification.

2.2. $[(\eta^5\text{-BuC}_5\text{H}_4)\text{Fe}(\text{CO})(\mu\text{-P:N-PPh}_2\text{Py})(\mu\text{-H})\text{Mo}(\text{CO})_4]$ **7a**

Compound **3** (0.30 g, 0.60 mmol) reacted with **6a** (0.30 g, 0.87 mmol) and were dissolved in dry THF (30 mL). The mixture was warmed up to ensure complete dissolution, to give orange solution. The mixture was then stirred at room temperature for 2 h to give a deep orange solution which was filtered via a pad of dry celite under nitrogen and washed with dry ether until colourless to give clear orange solution. The solvent was removed under vacuum. The ensuing orange solid was dissolved in a little quantity of CH_2Cl_2 and mixed well with a little quantity of Al_2O_3 before being packed on a short Al_2O_3 column. The orange band was eluted with 1:8–1:5 $\text{EtOAc}/n\text{-hexane}$ mixtures. Bright orange powder of **7a** was collected after removing the solvent under vacuum.

Compound **7a**: yield: 0.33 g, 81%; mp: 111 °C (dec.); IR (CH_2Cl_2) ν_{CO} 2016 (m), 1927 (vs), 1896 (s), 1879 (sh), 1830 (s) cm^{-1} ; ^{31}P NMR (CDCl_3) δ 86.12 (s); ^1H NMR (CDCl_3) δ 9.25 (b, 1H, Py), 6.93–7.68 (m, 13H, Ph and Py), 4.75, 4.66, 4.41, 4.30 ($4 \times$ b, $4 \times$ 1H, Cp), 0.87–2.42 (m, 9H, Bu), -16.46 (d, 1H, $\mu\text{-H}$, $^2J_{\text{PH}} = 56$ Hz); MS m/z 678 ($\text{M}^+ + 1$). Anal. Calc. for $\text{C}_{31}\text{H}_{28}\text{FeMoNO}_5\text{P}$: C, 54.95; H, 4.14; N, 2.07. Found: C, 55.24; H, 4.85; N 1.77%.

2.3. $[(\eta^5\text{-BuC}_5\text{H}_4)\text{Fe}(\text{CO})(\mu\text{-P:N-PPh}_2\text{Py})(\mu\text{-H})\text{W}(\text{CO})_4]$ **7b**

Compound **3** (0.30 g, 0.60 mmol) and **6b** (0.30 g, 0.69 mmol) were dissolved in dry THF (30 mL). The procedure is similar to that of the reaction of the molybdenum analogue except that the purification was carried out using a silica gel column. The orange solid was dissolved in a small quantity of CH_2Cl_2 and mixed well with a small quantity of silica gel before being packed on top of a silica gel column, and then eluted with a $\text{EtOAc}/n\text{-hexane}$ mixture. The orange powder of **7b** was collected after solvent removal under vacuum.

Compound **7b**: yield: 0.35 g, 76%, mp: 120 °C (dec.); IR (CH_2Cl_2) ν_{CO} 2009 (m), 1927 (s) 1886 (vs, b), 1827 (s) cm^{-1} ; ^{31}P NMR (CDCl_3) δ 88.6 (s); ^1H NMR (CDCl_3) δ 9.38 (b, 1H, Py), 6.90–7.48 (m, 13H, Ph and Py), 4.77, 4.72, 4.51, 4.31 ($4 \times$ b, $4 \times$ 1H, Cp), 0.87–2.63 (m, 9H, Bu), -14.21 (d, 1H, $\mu\text{-H}$, $^2J_{\text{PH}} = 54$ Hz); MS m/z 766 ($\text{M}^+ + 1$). Anal. Calc. $\text{C}_{31}\text{H}_{28}\text{FeNO}_5\text{PW}$: C, 48.63; H, 3.66; N, 1.83. Found: C, 48.78; H, 3.98; N, 1.75%.

2.4. $[(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\mu\text{-P:N,N'-PPhPy}_2)\text{Mo}(\text{CO})_4]$ **10a**

Compound **4** (0.10 g, 0.20 mmol) and **9a** (0.10 g, 0.31 mmol) were completely dissolved in dry THF (10 mL). The colour changed to blood red immediately. The mixture was allowed to stir for 1.5 h before filtration over a bed of dry celite under nitrogen. The solvent was removed under vacuum and the red solid re-crystallized twice

with ether/ n -hexane mixture (1:1) and filtered to give a brick red solid of **10a**. Using $(\text{C}_7\text{H}_8)\text{Mo}(\text{CO})_4$ (80 mg, 0.27 mmol, C_7H_8 = bicyclo [2,2] hepta-2,5-diene) to replace **9a**, the result is the same with very similar yields.

Compound **10a**: yield: 0.114 g, 81%, mp: 138 °C (dec.); IR (CH_2Cl_2) ν_{CO} 1977 (s), 1919 (vs) 1816 (s, b) cm^{-1} ; ^{31}P NMR (CDCl_3) δ 95.5 (s); ^1H NMR (CDCl_3) δ 9.24 (b, 2H, Py), $^4J_{\text{PH}} = 4.95$ Hz, 6.53–8.30 (m, 11H, Ph and Py), 4.95 (b, 2H, $-\text{CH}=\text{CHCHBu-}$), 2.49 (b, 1H, $-\text{CH}=\text{CHCHBu-}$), 2.22 (b, 2H, $-\text{CH}=\text{CHCHBu-}$), 0.51–1.08 (m, 9H, Bu), MS (m/z) 497 ($\text{M}^+ - \text{Mo}(\text{CO})_4 + 1$), 441 ($\text{M}^+ - \text{Mo}(\text{CO})_6 + 1$). Anal. Calc. $\text{C}_{31}\text{H}_{27}\text{FeMo-N}_2\text{O}_6\text{P}$: C, 52.69; H, 3.82; N, 3.97. Found: C, 52.16; H, 4.43; N, 3.65%.

2.5. $[(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\mu\text{-P:N,N'-PPhPy}_2)\text{W}(\text{CO})_4]$ **10b**

The procedure is similar to that of the reaction of the molybdenum analogue with **4** (0.30 g, 0.60 mmol) and **9b** (0.30 g, 0.74 mmol) in dry THF (10 mL). Dark purple solid of **10b** was collected after the necessary work-up.

Compound **10b** : yield: 0.40 g, 83%; mp: 143 °C (dec.); IR (CH_2Cl_2) ν_{CO} 1977 (s), 1912 (vs) 1813 (s, b) cm^{-1} ; ^{31}P NMR (CDCl_3) δ 97.9 (s); ^1H NMR (CDCl_3) δ 9.30 (b, 2H, Py), 6.40–8.28 (m, 11H, Ph and Py), 4.98 (b, 2H, $-\text{CH}=\text{CHCHBu-}$), 2.52 (b, 1H, $-\text{CH}=\text{CHCHBu-}$), 2.29 (b, 2H, $-\text{CH}=\text{CHCHBu-}$), 0.56–1.06 (m, 9H, Bu), MS m/z 767 ($\text{M}^+ - \text{CO} + 1$) 497, ($\text{M}^+ - \text{W}(\text{CO})_4 + 1$). Anal. Calc. for $\text{C}_{31}\text{H}_{27}\text{FeN}_2\text{O}_6\text{PW}$: C, 46.85; H, 3.40; N, 3.53. Found: C, 46.32; H, 3.66; N, 3.33%.

2.6. $[(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\mu\text{-P:N,N''-PPy}_3)\text{Mo}(\text{CO})_3]$ **12a**

Compound **5** (0.20 g, 0.40 mmol) and **6a** (0.20 g, 0.58 mmol) were completely dissolved in dry THF (20 mL). The mixture turned purple immediately. The reaction was left for 1 h before being filtered under nitrogen through a pad of dry celite and washed with dry ether until colourless. The solvent was removed under vacuum, resulting in a dark purple solid, which was dissolved in a small quantity of CH_2Cl_2 and mixed completely with a small quantity of alumina. The CH_2Cl_2 was removed under vacuum. The residue was packed on top of an alumina column and then eluted with a 3:1 $\text{EtOAc}/n\text{-hexane}$ mixture. A deep purple solid **12a** was collected.

Compound **12a**: yield: 0.26 g, 96%; mp: 158 °C (dec.); IR (CH_2Cl_2) ν_{CO} 1981 (m), 1924 (m), 1905 (vs), 1788 (s, b) cm^{-1} ; ^{31}P NMR (CDCl_3) δ 75.4 (s); ^1H NMR (CDCl_3) δ 9.47 (b, 3H), 8.48 (b, 3H), 7.85 (b, 3H), 7.20 (b, 3H) for pyridine, 5.35 (b, 2H, $-\text{CH}=\text{CHCHBu-}$), 3.27 (b, 2H, $-\text{CH}=\text{CHCHBu-}$), 3.04 (b, 1H, $-\text{CH}=\text{CHCHBu-}$), 0.83–1.15 (m, 9H, Bu), MS m/z 498 ($\text{M}^+ - \text{Mo}(\text{CO})_3$). Anal. Calc. $\text{C}_{29}\text{H}_{25}\text{FeMoN}_3\text{O}_5\text{P}$: C, 51.33; H, 3.69; N, 6.19. Found: C, 50.38; H, 3.95; N, 5.73%.

2.7. $[(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\mu\text{-P:N,N''-PPy}_3)\text{W}(\text{CO})_3]$ **12b**

Compound **5** (0.20 g, 0.40 mmol) and **6b** (0.20 g, 0.46 mmol) were dissolved in dry THF (10 mL). Again the mixture immediately changed to purple colour. The reaction was then left for 2 h. Other procedure and work-up were similar to those used in the molybdenum analogue.

Compound **12b**: yield: 0.24 g, 78%; mp: 165 °C (dec.); IR (CH_2Cl_2) ν_{CO} 1982 (m), 1926 (s), 1895 (vs), 1782 (s, b) cm^{-1} ; ^{31}P NMR (CDCl_3) δ 77.2 (s); ^1H NMR (CDCl_3) δ 9.48 (b, 3H) 8.50 (b, 3H), 7.88 (b, 3H), 7.15 (b, 3H) for pyridine, 5.38 (b, 2H, $-\text{CH}=\text{CHCHBu-}$), 3.31 (b, 2H, $-\text{CH}=\text{CHCHBu-}$), 3.06 (b, 1H, $-\text{CH}=\text{CHCHBu-}$), 0.82–1.24 (m, 9H, Bu); MS m/z 498 ($\text{M}^+ - \text{W}(\text{CO})_3$). Anal. Calc. for $\text{C}_{29}\text{H}_{25}\text{FeN}_3\text{O}_5\text{PW}$: C, 45.43; H, 3.26; N, 5.43. Found: C, 44.98; H, 3.63; N, 5.00%.

3. Results and discussion

3.1. Preparation of arylpyridylphosphine ligands

The preparation of $\text{PPh}_{3-n}\text{Py}_n$ ($n = 1-3$) followed the literature procedures but with a slight local modification [8a,8b,8c]. In our own experience, the preparation of PPhPy_2 gave a yield of 19.7% when the Grignard reagent on the pyridyl side is used for coupling with PPhCl_2 . The preparation of PPhPy_2 gave a much better yield of 54.5% by using the Li–Br exchange reaction between $n\text{-BuLi}$ and $o\text{-C}_5\text{H}_4\text{NBr}$, then the coupling reaction with PPhCl_2 . The preparation of $\text{PPh}_{3-n}\text{Py}_n$ ($n = 1-3$) in the present study involved the $n\text{-BuLi}$ route and the yields were satisfactory (PPh_2Py , 82%; PPhPy_2 , 55%; PPy_3 , 62%). Pure PPy_3 was stored in the dry box in order to avoid oxidation of the phosphine to $\text{Py}_3\text{P=O}$.

3.2. $(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_{3-n}\text{Py}_n)$ complexes

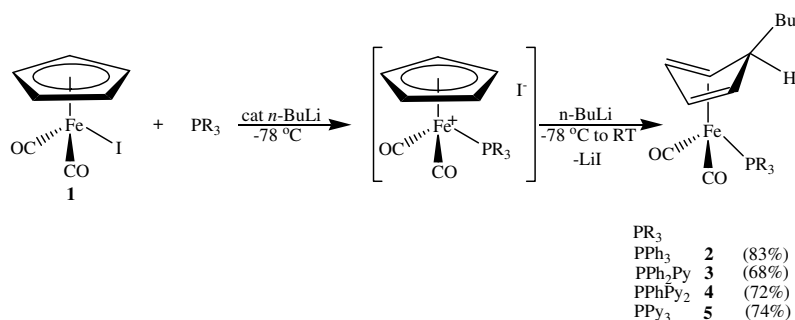
The arylpyridylphosphine ligands were reacted with a stoichiometric amount of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ (**1**) and a slight excess amount of $n\text{-BuLi}$, using the same conditions as those used in the preparation of $(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)$ (**2**) [3]. With one basic N-atom in each pendant pyridine, the arylpyridylphosphines reacted smoothly in the three-component reaction and gave similarly $(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_{3-n}\text{Py}_n)$ in good yields of relevant

complexes (**3**, $n = 1$, 68%; **4**, $n = 2$, 72%; **5**, $n = 3$, 74%). The chemistry followed the same pathway as in the PPh_3 case [3].

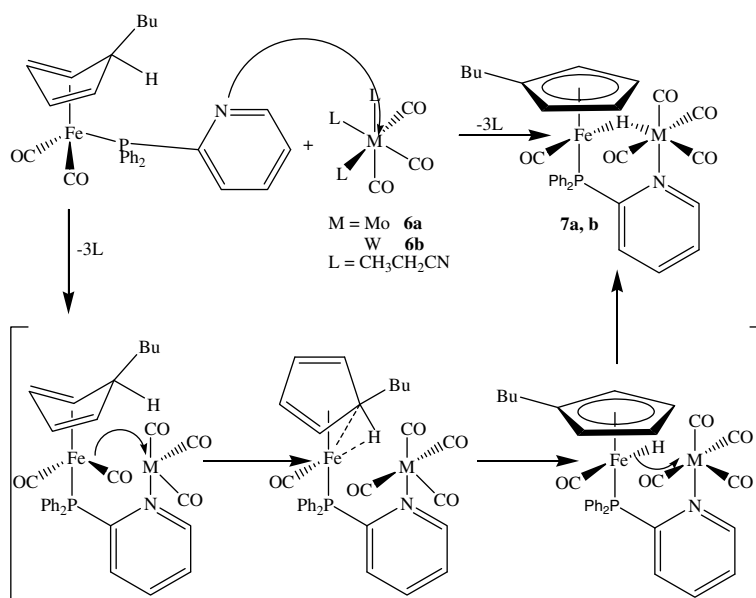
Scheme 1 shows the two stages in the three-component preparation of compounds **2–5**. The first drop of $n\text{-BuLi}$ acted as a reducing agent [9] to initiate an electron-transfer chain catalysis [10] of the replacement of iodide on **1** by $\text{PPh}_{3-n}\text{Py}_n$ with the P-donor mode. The cation $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_{3-n}\text{Py}_n)^+]$ ($n = 0-4$) is instantaneously obtained in this reaction [11]. The stoichiometric $n\text{-BuLi}$ then acts as a normal nucleophile to add on to the $(\eta^5\text{-C}_5\text{H}_5)$ -ring [12,13]. The electron rich $(\eta^5\text{-C}_5\text{H}_5)$ -ring of neutral **1** did not react with the electron rich $[\text{Bu}^-]$ anion in an ordinary way. In its cationic form, the $(\eta^5\text{-C}_5\text{H}_5)$ -ring is more likely activated as a Lewis-acid. $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_{3-n}\text{Py}_n)^+]$ is much more electrophilic towards $[\text{Bu}^-]$ and the addition of $[\text{Bu}^-]$ anion on the $(\eta^5\text{-C}_5\text{H}_5)$ -ring is favoured [3].

3.3. Heterodimetallic complexes

In the main synthetic routes to organo-transition metal hydrides, the intramolecular oxidative addition is a key to the facile loss of hydrogen, for example, in $(\eta^4\text{-C}_5\text{H}_6)\text{Fe}(\text{CO})_3$ which proceeds with an intermediate formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$, to finally yield $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}_2$ [14]. Yet, it is possible to independently synthesize $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$ from the acidification of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Na}$. In the literature, it was not synthesized directly



Scheme 1.



Scheme 2.

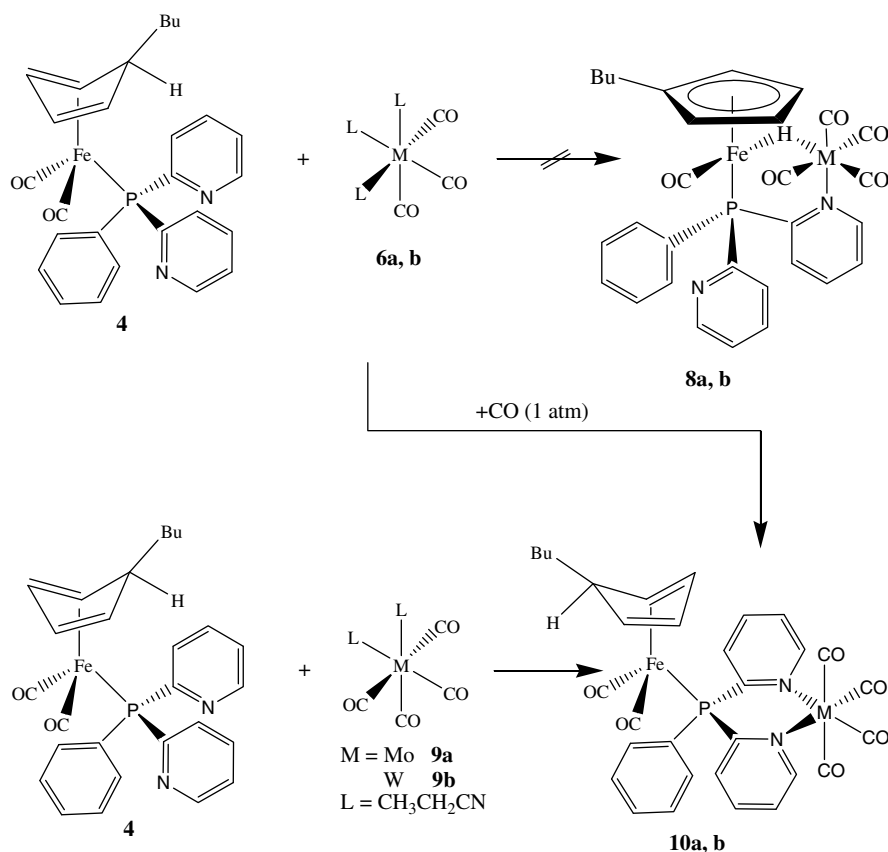
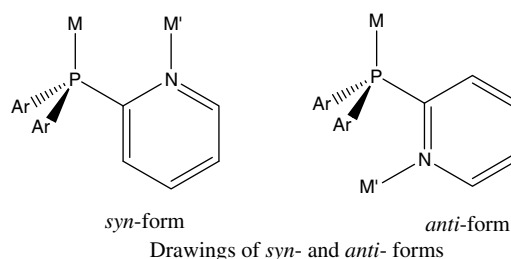
from $(\eta^4\text{-C}_5\text{H}_6)\text{Fe}(\text{CO})_3$ due to competing and/or consecutive reactions [15].

We discuss below a clean activation of the *endo*-C–H bond of **3** that was formally a $(\eta^4\text{-cyclopentadiene})\text{-Fe}$ complex in PPh_2Py derivative. When **3** is reacted with $\text{M}(\text{CO})_3(\text{EtCN})_3$ ($\text{M} = \text{Mo}$, **6a**; W , **6b**) with the labile EtCN to be replaced by the pyridyl N-atom and others, the result is the hydridobridged heterodimetallic complex $[(\eta^5\text{-BuC}_5\text{H}_4)\text{Fe}(\text{CO})(\mu\text{-P:}N\text{-PPh}_2\text{Py})(\mu\text{-H})\text{M}(\text{CO})_4]$ ($\text{M} = \text{Mo}$, **7a**, 81%; W , **7b**, 76%) with six-membered heterocyclic ring (Scheme 2).

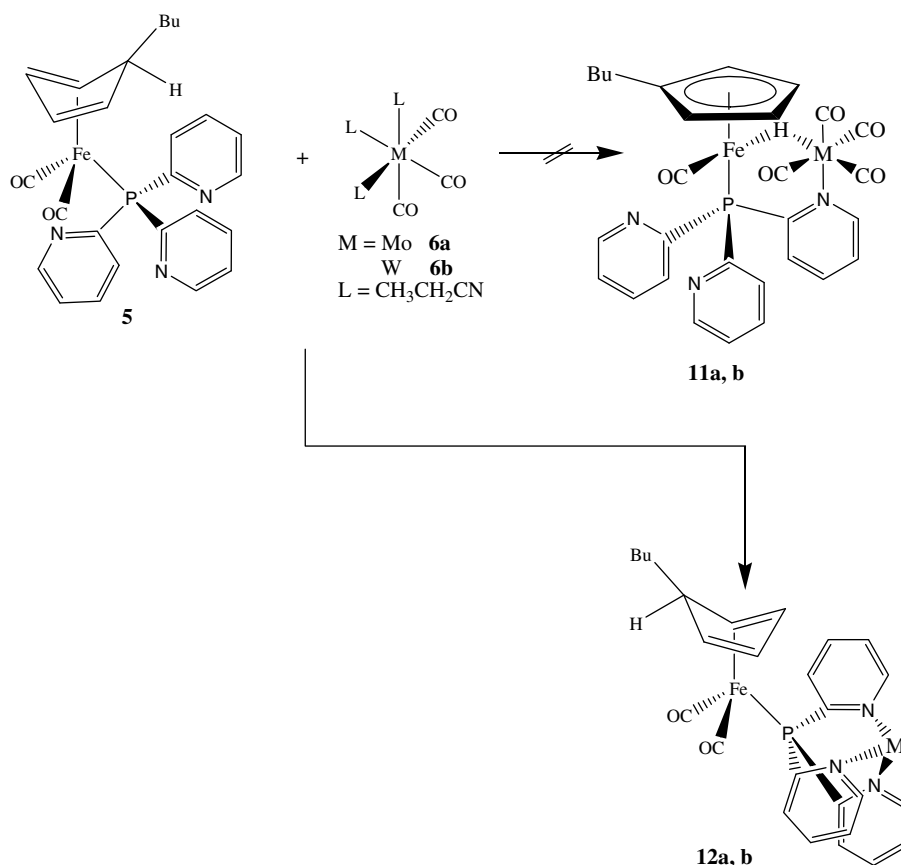
The environments around Fe and M in **7a,b** changed substantially from the starting environments of **3** and **6a,b** as shown by the complete disappearance of all the original IR ν_{CO} bands: the 1966 (s) cm^{-1} bands for the two CO ligands connected to Fe in **3**, the 1921 (s), 1801 (s) cm^{-1} for the three CO ligands connected to Mo in **6a**, and the 1910 (s), 1793 (s) cm^{-1} for the three CO ligands connected to W in **6b**. The ^1H NMR data also indicated that the 2:1:2 integration ratios for the $(\eta^4\text{-BuC}_5\text{H}_5)$ fragment of **3** disappeared. Whereas a 4-peak, equal-intensity pattern characteristic of a $(\eta^5\text{-BuC}_5\text{H}_4)$ connected to a chiral metal centre appeared (cf. at δ 4.75, 4.66, 4.41, 4.30 in **7a** and at δ 4.77, 4.72, 4.51, 4.31 in **7b**). The doublet hydrides at δ –16.5 with $^2J_{\text{PH}} = 56$ Hz in **7a** and at δ –14.2 with $^2J_{\text{PH}} = 54$ Hz in **7b** were observed in the ^1H NMR spectra. The molecular structure of **7a,b** was finalized on the basis of a similar compound $[(\eta^4\text{-MeC}_5\text{H}_4)\text{Fe}(\text{CO})(\mu\text{-P:P'}\text{-PPh}_2\text{CH}_2\text{PPh}_2)(\mu\text{-H})\text{M}(\text{CO})_4]$ ($\text{M} = \text{Mo}$ and W) [16] that was prepared from **6a,b** and a $[(\eta^4\text{-MeC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-PPh}_2\text{CH}_2\text{PPh}_2)]$ with the dangling PPh_2 working the same way as the present pyridyl N-atom. The dppm analogue revealed very similar spectroscopic data in the IR and ^1H NMR spectra to those of **7a,b**, especially those of the hydride and $(\eta^5\text{-MeC}_5\text{H}_4)$ ligands connected to a chiral metal centre. Earlier, the origin of the hydride and additional CO on M-centre of $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Fe}(\text{CO})(\mu\text{-P:P'}\text{-PPh}_2\text{CH}_2\text{PPh}_2)(\mu\text{-H})\text{M}(\text{CO})_4]$ ($\text{M} = \text{Mo}$

and W) [16] was assigned as intramolecularly converted from the *endo*-H and the CO on Fe-centre, based on quantitative yield during synthesis. The hydride remained un-changed with the deuterium atoms of *d*-solvent when the reaction was performed in $d^8\text{-THF}$. It is pertinent to state that, crystal suitable for X-ray crystallography for these compounds was attempted, but did not succeed.

Apparently in Scheme 2, it shows that, upon pyridyl N-atom ligation to the second metal ($\text{M} = \text{Mo}$, W), this neighbouring metal M induces an oxidative addition of the *endo*-C–H of cyclopentadiene on the initial Fe-centre, by taking away a CO ligand from the Fe-centre. Originally the Fe-centre in **3** is penta-coordinate. The loss of CO to M-centre results in a tetra-coordinate Fe(0), ready to activate the nearby *endo* C–H bond. Along the reaction coordinate, Fe(0) then changes to a hexa-coordinate Fe(II). At a later stage, the second metal M traps the newly formed Fe–H bond in the form of “3c–2e” M–H–Fe structure. The relative conformation with respect to Fe and M is not yet clear during the stage of the pyridyl N-atom ligation or during the stage of the CO-migration. The final conformation with respect to Fe and M is in a *syn*-form in **7a,b**.



Scheme 3.



Scheme 4.

With two pyridyl N-atoms, **4** gave no hydride formation when it was reacted with **6a,b**. There was no spectroscopic evidence to support the structure $[(\eta^5-BuC_5H_4)Fe(CO)(\mu-P:N-PPhPy_2)(\mu-H)-M(CO)_4]$ ($M = Mo$, **8a**; W , **8b**) (Scheme 3).

When **4** was treated with $M(CO)_4(EtCN)_2$ ($M = Mo$, **9a**; W , **9b**) as shown in Scheme 3, the N,N' -chelated heterodimetallic complex was collected in high yield, i.e., $[(\eta^4-BuC_5H_5)Fe(CO)_2(\mu-P:N,N'-PPhPy_2)M(CO)_4]$ ($M = Mo$, **10a**, 81%; W , **10b**, 83%) ($C_7H_8 =$ bicyclo [2,2] hepta-2,5-diene) replacing **9a** gave the same result). Alternative route to the synthesis of **10a, b** was achieved when CO (1 atm) was bubbled into the solution of **4** and **6a,b** to produce variable yields of **10a,b**.

The reaction of **5** and **6a,b** shown in Scheme 4, did not give compound $[(\eta^5-BuC_5H_4)Fe(CO)(\mu-P:N-PPy_3)(\mu-H)M(CO)_4]$ ($M = Mo$, **11a**; W , **11b**), but the N,N',N'' -coordinated heterodimetallic complex $[(\eta^4-BuC_5H_5)Fe(CO)_2(\mu-P:N,N',N''-PPy_3)M(CO)_3]$ ($M = Mo$, **12a**, 96%; W , **12b**, 78%).

The IR ν_{CO} data for the two CO ligands connected to Fe exhibit a shift to higher wave numbers upon attachment of $M(CO)_3$ to the three pyridyl N-sites of PPy_3 , i.e., from 1969, 1909 cm^{-1} in **5** to 1981, 1924 cm^{-1} in **12a** and 1982, 1926 cm^{-1} in **12b**. Upon attachment of $M(CO)_4$ to the two pyridyl N-sites of $PPhPy_2$, similar shifts are found in **10a,b**, to 1977, 1919 cm^{-1} and 1977, 1912 cm^{-1} , respectively, comparing with 1967, 1907 cm^{-1} in **4**. It was observed that, complexes **10a,b** and **12a** were not excellently stable when expose to air. This could attributes to high values recorded for carbon in the elemental analysis results.

4. Conclusion

Organo-transition metal hydrides could be produced through the intramolecular oxidative addition reaction between *endo*-C–H

of cyclopentadiene iron with one pyridyl N-atom and $M(CO)_3L_3$ ($M = Mo$, W ; $L =$ labile ligand). Yet, there is no hydride formation with complexes of more than one pyridyl N-atoms e.g. $(\eta^4-BuC_5H_5)Fe(CO)_2(PPhPy_2)$ and $(\eta^4-BuC_5H_5)Fe(CO)_2(PPy_3)$. The CO transfer from Fe to M shown in Scheme 2 is more likely to be the slow step than the pyridyl N-ligation to M, to the state, ready for oxidative addition of Fe(0) in the reaction coordinate. Apparently, in **4** and **5**, extra pyridyl N-atom(s) are involved to mask the migration of CO ligand from Fe-centre to M-centre. Accordingly, these two compounds do not exhibit an induced activation of the *endo*-C–H bond of the cyclopentadiene on Fe-centre.

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