

Preliminary communication

ELECTRON-RICH, HYDROCARBON-METAL COMPLEXES: SYNTHESIS AND OXIDATION PROPERTIES OF BIS(η^3 -ALLYL) IRON COMPLEXES CONTAINING BASIC PHOSPHINES

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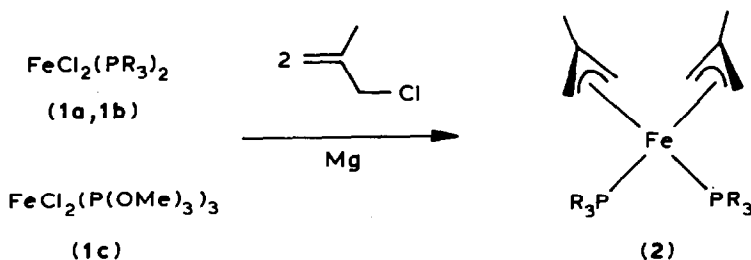
Summary

Methallyl chloride and $\text{FeCl}_2(\text{PR}_3)_n$ react in the presence of magnesium to give $\text{Fe}(\eta^3\text{-2-Me-allyl})_2(\text{PR}_3)_2$ complexes (**2**) in good yield [**2a** PMe_3 (70%); **2b** PMe_2Ph (80%); **2c** P(OMe)_3 (51%)]. Reaction of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{M}$ ($\text{M} = \text{Li}, \text{K}$) with $\text{FeCl}_2(\text{PR}_3)_2/\text{PR}_3$ gives a mixture of **2** and (trimethylenemethane) $\text{Fe}(\text{PR}_3)_3$. Cyclic voltammetry of the complexes **2** shows that oxidation occurs at negative potentials (-0.52 (**2a**), -0.37 V vs. SCE (**2b**)), is irreversible at room temperature, and becomes reversible at low temperature. Complexes **2a,2b** react with an excess of NOBF_4 to give the complexes $\text{Fe}(\text{NO})_2(\text{PR}_3)_2$.

Most of the characterized allylmetal complexes in the Fe, Ru, Os triad, contain additional electron-withdrawing ligands such as carbonyls [1–5]. Although electron-rich hydrocarbon-metal complexes have recently attracted interest, especially in connection with radical promoted reactions [6–8], very few electron-rich allyliron or allylruthenium complexes containing very basic ligands have been described, probably because of the non-availability of a general or direct route to such compounds. However, $\text{Ru}(2\text{-Me-allyl})_2(\text{P(OR)}_3)_2$ [9] derivatives have been prepared from $\text{Ru}(2\text{-Me-allyl})_2(\text{COD})$ and recently an unsymmetrical $\text{Fe}(\eta^3\text{-allyl})_2\text{Fe}(\text{PMe}_3)_2$ [10] was obtained by reaction of potassium pentadienide with an iron(II) precursor.

We now report a simple route to electron-rich allyliron complexes, $\text{Fe}(\eta^3\text{-allyl})_2(\text{PR}_3)_2$ directly from methallyl chloride and FeCl_2 , involving an approach based on our method of making trimethylenemethane iron derivatives [6]. The allyl iron compounds undergo oxidation at negative potentials [4] and can be used as a source of the “ $\text{Fe}(\text{PR}_3)_2$ ” moiety for access to $\text{Fe}(\text{NO})_2(\text{PR}_3)_2$ derivatives.

The complexes $\text{FeCl}_2(\text{PR}_3)_2$ (**1a,1b**) [11] and $\text{FeCl}_2(\text{P(OMe)}_3)_3$ (**1c**) [12] were prepared in THF directly from FeCl_2 and treated in situ with two equivalents of methallyl chloride and an excess of magnesium at room temperature for 2 h. Air-sensitive complexes were isolated as yellow solids after filtration of the solution



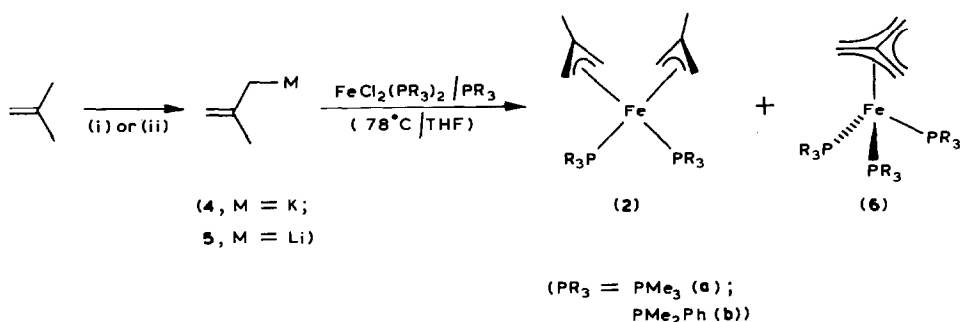
$(\text{PR}_3 = \text{PMe}_3 \text{ (a)};$
 $\text{PMe}_2\text{Ph} \text{ (b)};$
 $\text{P}(\text{OMe})_3 \text{ (c)})$

SCHEME 1.

through a short column of silicagel, and were identified as **2a** (70%), **2b** (80%), and **2c** (51%), respectively, (Scheme 1) which gave satisfactory C, H, and P analyses. The ^1H , ^{31}P and ^{13}C NMR spectra establish the equivalence of the two phosphorus ligands in complexes **2a–2c**. The shape of the ^1H resonances, assigned respectively to the methyl and methoxy groups attached to the P atoms, is consistent with an $\text{H}_9\text{PP}'\text{H}'_9$ system with a *cis*-arrangement of the two phosphorus nuclei. The $\{^1\text{H}\}^{13}\text{C}$ NMR spectra of **2a** and **2c** show four signals for the methallyl carbon nuclei, ($\{^1\text{H}\}^{13}\text{C}$ NMR (75.45 MHz, 300 K) for **2a**: δ 90.4 (C(2)), 43.4 (H_2C (3)), 39.2 (H_2C (1)), 26.3 (CH_3C (2)), 19.4 (d, $\text{P}(\text{CH}_3)_3$, $^1J(\text{PC})$ 38 Hz) which is consistent with the presence of equivalent methallyl ligands in complexes **2** but with different methylene groups in each methallyl group. We could suggest for complexes **2** a structure analogous to that reported for $\text{Fe}(\eta^3\text{-CH}_2\text{=CH=CH-CH=CH}_2)_2(\text{PMe}_3)_2$ [10] but, the latter complex contains unsymmetrical allyl ligands and the NMR data for **2** indicate that in these complexes containing symmetrically substituted (η^3 -2-Me-allyl) ligands the dissymmetry of the allyl ligands is essentially due to bonding rather than to substitution.

It is noteworthy that complexes **2a** and **2b** were obtained in only 10% yield when two equivalents of the methallyl magnesium chloride were added to **1a** and **1b**. It is likely that when the Grignard reagent is made in situ, the transmetalation of its allyl group to the iron is rapid compared with its decomposition.

We also investigated the possibility of preparing complexes **2** from an olefin (isobutene), via the addition of the corresponding potassium **4** and lithium **5** derivatives to **1**. In fact, complexes **2** and **6** [6] were formed together (Scheme 2). Thus, addition of **1a**/ PMe_3 (1/1) in THF to one equivalent of **4** in pentane, or of **5** in hexane, led to a mixture of **2a**/**6a** (75/25) in approximately 70% yield. A mixture of **2b**/**6b** (70/30) was also obtained similarly from **1b**/ PMe_2Ph in 80% yield. When the accompanying *t*-BuOLi was removed from **5** before treatment with **1a**/ PMe_3 , only **2b** was formed. Furthermore, complex **2a** did not react with *n*-BuLi, *t*-BuOK or *t*-BuOLi to give **6a**. These two observations suggest that the formation of **6** from **1**/ PMe_3 results from deprotonation or reduction by *t*-BuOLi of the reaction intermediate leading to **2**. These results show the advantage of the route **1** \rightarrow **2**, via allyl halide and magnesium over that using potassium or lithium isobutenide. The

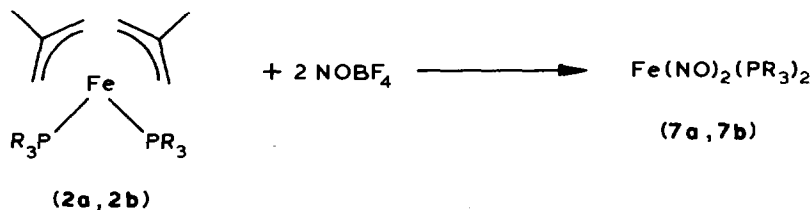


SCHEME 2. (i): n-BuLi/t-BuOK in pentane; (ii) n-BuLi/TMEDA in hexane.

formation of **6** from **1** represents a new route to an electron-rich trimethylenemethane-metal complex directly from a substituted olefin.

The complexes **2** were studied by cyclic voltammetry in order to assess their electron-rich character. With a platinum electrode, cyclic voltammetry of complexes **2** in acetonitrile at room temperature showed, in the range -1.5 to $+1.5$ V vs. SCE, only one irreversible wave of oxidation at low potential [E_p^a (V vs. SCE): -0.52 (**2a**); -0.37 (**2b**); $+0.05$ (**2c**)]. The oxidation potential depends on the electron donor ability of the phosphorus ligands. The E_p^a values reveal the electron-rich character of the complexes **2**, since they fall midway between the corresponding values for the electron-rich iron(II) complexes **6** [E_p^a : -0.42 (**6a**); -0.33 (**6b**) V vs. SCE] and the iron(0) derivatives (η^4 -diene) $Fe(PR_3)_3$ [E_p^a : -0.61 (PMe_3); -0.48 (PMe_2Ph) V vs. SCE]. There was no oxidation at positive potentials such as would be expected for the oxidation of any free phosphines [**6**] formed by decomposition of **2**, and the resulting 17-electron cation was expected to be stable. Cyclic voltammetry of complex **3a** at $-35^\circ C$ in acetonitrile but with an Ag/AgNO₃ reference electrode, showed a reversible oxidation ($E_p^a = -0.87$ V; $E_p^c = -0.94$ V; $v = 0.2$ V s⁻¹), and when the temperature was allowed to rise to $0^\circ C$, the reduction peak decreased progressively.

The facile oxidation of complexes **2a, 2b** led us to investigate their reaction with NOBF₄ in acetonitrile. With two equivalents of NOBF₄ **2a** and **2b** gave respectively **7a** (48%; IR, 1710, 1660 cm⁻¹; ³¹P NMR (32.38 MHz): 13.67 ppm (s)) and **7b** (58%, IR, 1720, 1670 cm⁻¹; ³¹P NMR (32.38 MHz): 25.69 ppm (s)), (Scheme 3). Although analogous Fe(NO)₂(PAr₃)₂ derivatives have been reported [13], the complexes **2**

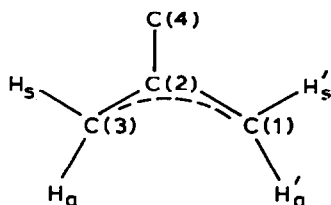


SCHEME 3.

provide a good starting points for preparation of $\text{Fe}(\text{NO})_2(\text{PR}_3)_2$ complexes containing alkylphosphines in a one pot reaction from FeCl_2 , via complexes **1**. This procedure demonstrates the potential of the easily oxidized $\text{Fe}(\text{allyl})_2(\text{PR}_3)_2$ as a source of the " $\text{Fe}(\text{PR}_3)_2$ " species.

Data for the characterization of complexes 2 and 7

For the assignments of the NMR data, the allyl groups have been numbered as follows. The more shielded C(1), H_s' and H_a' nuclei are expected to be closer to the iron atom than C(1), H_s and H_a. The letter s and a stand for *syn* and *anti* with respect to the C(4) or the H(C(2)) atom.



2a: Anal. Found: C, 53.24; H, 9.98; P, 19.41. $\text{C}_{14}\text{H}_{32}\text{P}_2\text{Fe}$ calcd.: C, 52.83; H, 10.06; P, 19.49%. Mass spectrum: m/e : 318.133 (calcd. for M^+ : 318.133). ^1H NMR (80 MHz, C_6D_6 , 305 K) δ 2.06 (s, CH_3C), 1.52 (m, H_s), 1.25 (m, H_s'), 0.97 (t, PMe_3 , $|^2J(\text{PH}) + 4J(\text{P}'\text{H})|$ 5.9 Hz), 0.50 (m, H_a, $|^2J(\text{PH}) + ^2J(\text{P}'\text{H})|$ 17.6 Hz), -0.37 (m, H_a', $|^2J(\text{PH}) + ^2J(\text{P}'\text{H})|$ 21.3 Hz). ^{31}P NMR 32.38 MHz, C_6D_6 , 310 K), δ 26.0 (s). $\{^1\text{H}\}^{13}\text{C}$ NMR (75.45 MHz, C_6D_6 , 300 K) δ 90.4 (C(2)), 43.4 (H₂C(3)), 39.2 (H₂C(1)), 26.3 ($\text{CH}_3\text{C}(2)$), 19.4 (d, P (CH_3)₃, $^1J(\text{PC})$ 38 Hz); ^{13}C NMR δ 90.4 (s), 43.4 (t, $^1J(\text{CH})$ 148 Hz), 39.2 (t, $^1J(\text{CH})$ 151 Hz), 26.3 (q, $^1J(\text{CH})$ 125 Hz) 19.4 (q, $^1J(\text{CH})$ 127 Hz).

2b: Anal. Found: C, 64.80; H, 8.06; P, 13.95; Fe, 12.17. $\text{C}_{24}\text{H}_{36}\text{P}_2\text{Fe}$ calcd.: C, 65.15; H, 8.14; P, 14.02; Fe, 12.07%. Mass spectrum: m/e : 442.163 (calcd. for M^+ : 442.164). ^1H NMR (300 MHz, toluene- d_8 , 305 K) δ 7.09 (m, C_6H_5), 2.04 (s, CH_3C), 1.94 (m, H_s), 1.20 (m, H_s') 1.31 (br s), $\text{PCH}_3(\text{A})$ and 1.12 (br s), $\text{PCH}_3(\text{B})$ 0.41 (m, H_a, $|J(\text{PH}) + J(\text{P}'\text{H})|$ 16.7 Hz), -0.22 (m, H_a', $|J(\text{PH}') + J(\text{P}'\text{H}')|$ 19.8 Hz). ^{31}P NMR (32.38 MHz, C_6D_6 , 310 K) δ 33.4 (s). $\{^1\text{H}\}^{13}\text{C}$ NMR (20.115 MHz, C_6D_6 , 310 K) δ 92.3 (s, C(2), 43.6 (t, C(3), $|J(\text{PC}) + J(\text{P}'\text{C})|$ 18 Hz), 40.8 (t, C(1), $|J(\text{PC}) + J(\text{P}'\text{C})|$ 22 Hz), 26.8 (s, $\text{H}_3\text{C}(4)$), 20.6 (t, $\text{PCH}_3(\text{A})$, $|J(\text{PC}) + J(\text{P}'\text{C})|$ 29 Hz), 17.1 (t, $\text{PCH}_3(\text{B})$, $|J(\text{PC}) + J(\text{P}'\text{C})|$ 22 Hz).

2c: Mass spectrum: m/e 414.100 (calcd. for M^+ ($\text{C}_{14}\text{H}_{32}\text{O}_6\text{P}_2\text{Fe}$): 414.102; 383 ($M - \text{OCH}_3$)⁺; 359 ($M - \text{C}_4\text{H}_7$)⁺; 290 [$M - (\text{P}(\text{OMe})_3)$]⁺. ^1H NMR (80 MHz, C_6D_6 , 305 K), δ 3.51(t, $\text{P}(\text{OMe})_3$, $|^3J(\text{PH}) + ^3J(\text{P}'\text{H})|$ 10 Hz), 2.12 (s, CH_3C), 2.10 (m, H_s), 1.48 (m, H_s'), 1.45 (t, H_a, $|J(\text{PH}) + J(\text{P}'\text{H})|$ 17.0 Hz), 0.86 (m, H_a', $|J(\text{PH}) + J(\text{P}'\text{H})|$ 16.4 Hz). ^{31}P NMR (32.38 MHz, C_6D_6 , 310 K), δ 183.7 (s).

7a: IR (Nujol): 1710, 1660 cm^{-1} mass spectrum, m/e : 268.018 (calcd. for M^+ ($\text{C}_6\text{H}_{18}\text{N}_2\text{O}_2\text{P}_2\text{Fe}$): 268.019); ^1H NMR (80 MHz, CD_2Cl_2 , 305 K): δ 1.40 ppm (t, $|J(\text{PH}) + J(\text{P}'\text{H})|$ 8 Hz). ^{31}P NMR (32.38 MHz, CD_2Cl_2 , 310 K), δ 13.67 ppm (s).

7b: IR (Nujol): 1720, 1670 cm^{-1} , mass spectrum: m/e : 392.050 (calcd. for M^+ ($\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_2\text{P}_2\text{Fe}$): 392.050); ^1H NMR (80 MHz, CD_2Cl_2 , 307 K) δ (ppm): 7.34 (Ph), 1.48 (d, $J(\text{PH})$ 7.3 Hz). ^{31}P NMR (32.38 MHz, CD_2Cl_2 , 293 K) δ 25.69 ppm (s).

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