

Cationic Allyldinitrosyl Complexes of Iron †

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The nitrosonium salt $[\text{NO}][\text{PF}_6]$ reacts with $[\text{Fe}(\text{CO})\text{L}(\text{NO})(\eta^3\text{-allyl})]$ [$\text{L} = \text{P}(\text{OPh})_3, \text{P}(\text{OMe})_3, \text{or PPh}_3$; allyl = $\text{C}_3\text{H}_5, \text{C}_3\text{H}_4\text{Me-1}, \text{or C}_3\text{H}_4\text{Me-2}$] to give $[\text{FeL}(\text{NO})_2(\eta^3\text{-allyl})][\text{PF}_6]$. Spin saturation transfer ^1H n.m.r. spectroscopy shows that the fluxionality of the products involves slow allyl rotation at room temperature.

The substitution of CO by $[\text{NO}]^+$ provides a route by which the co-ordinated hydrocarbon of a neutral organometallic carbonyl complex can be activated towards nucleophilic attack. Thus, for example, $[\text{Mn}(\text{CO})_2(\text{NO})(\eta^3\text{-C}_6\text{H}_6\text{R})]^+$ ($\text{R} = \text{Me}$ or Ph)¹ and $[\text{Mo}(\text{CO})(\text{NO})(\eta^3\text{-C}_8\text{H}_{13})(\eta\text{-C}_5\text{H}_4\text{R})]^+$ [$\text{C}_8\text{H}_{13} = \text{cyclo-octenyl}, \text{R} = \text{neomenthyl (}i\text{-}2\text{-isopropyl-}i\text{-}5\text{-methylcyclohexan-}r\text{-1-yl)}$],² prepared from the appropriate carbonyls, have been used in the stereo- and regio-selective synthesis of disubstituted cyclohexadienes and the asymmetric synthesis of substituted cyclo-octenes respectively.

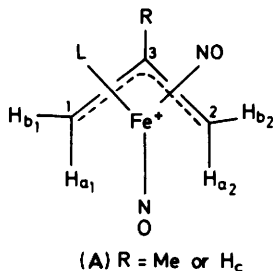
We now give details³ of the isolation of $[\text{FeL}(\text{NO})_2(\eta^3\text{-allyl})][\text{PF}_6]$ [$\text{L} = \text{P}(\text{OPh})_3, \text{P}(\text{OMe})_3, \text{or PPh}_3$; allyl = $\text{C}_3\text{H}_5, \text{C}_3\text{H}_4\text{Me-1}, \text{or C}_3\text{H}_4\text{Me-2}$], from $[\text{Fe}(\text{CO})\text{L}(\text{NO})(\eta^3\text{-allyl})]$ and $[\text{NO}][\text{PF}_6]$, and of the fluxional properties and reactions of the allyldinitrosyl cations.

Results and Discussion

The addition of solid $[\text{NO}][\text{PF}_6]$ to $[\text{Fe}(\text{CO})\text{L}(\text{NO})(\eta^3\text{-allyl})]$ [$\text{L} = \text{P}(\text{OPh})_3, \text{P}(\text{OMe})_3, \text{or PPh}_3$; allyl = $\text{C}_3\text{H}_5, \text{C}_3\text{H}_4\text{Me-1}, \text{or C}_3\text{H}_4\text{Me-2}$] in CH_2Cl_2 results in the evolution of CO gas and the formation of yellow to orange solutions; on filtration and addition of diethyl ether, moderate to good yields of the yellow ($\text{L} = \text{PPh}_3$) or orange [$\text{L} = \text{P}(\text{OPh})_3$ or $\text{P}(\text{OMe})_3$] crystalline salts $[\text{FeL}(\text{NO})_2(\eta^3\text{-allyl})][\text{PF}_6]$ (1) are precipitated.

The triphenylphosphine complexes (1; $\text{L} = \text{PPh}_3$) are very air-sensitive in solution, and also rapidly decompose in the solid state in air. They have been characterised only by i.r. spectroscopy and by analogy with the more thermally stable phosphite derivatives (Table 1) which may be readily stored, for prolonged periods in the solid state, under nitrogen at 0 °C.

The low-temperature n.m.r. spectra (Table 2) of complexes (1) are only compatible with the presence in solution of one, asymmetric isomer, (A). For example, the ^{13}C n.m.r. spectrum of



[1; $\text{L} = \text{P}(\text{OMe})_3$, allyl = C_3H_5] shows three resonances for the allyl carbon atoms, one coupled to the *trans*-phosphorus atom, and the ^1H n.m.r. spectra of (1) show separate resonances for each of the terminal allyl protons. The lower-frequency

signals in the ^1H n.m.r. spectra of complex [1; $\text{L} = \text{P}(\text{OPh})_3$ or $\text{P}(\text{OMe})_3$, allyl = C_3H_5] can be assigned to the *anti*-protons H_a because of the large couplings (12–14 Hz) to the central proton H_c . In addition the coupling of only one of the *anti*-protons to phosphorus further supports the asymmetric structure (A). In the case of [1; $\text{L} = \text{P}(\text{OMe})_3$, allyl = $\text{C}_3\text{H}_4\text{Me-1}$], the allyl methyl group is found exclusively in the *anti* position *trans* to phosphorus (Table 2).

At 30 °C, the terminal allyl resonances of complex [1; $\text{L} = \text{P}(\text{OPh})_3$, allyl = C_3H_5 or $\text{C}_3\text{H}_4\text{Me-2}$] broaden considerably but coalescence is not observed at higher temperatures, because of sample decomposition. Nevertheless, spin saturation transfer experiments with [1; $\text{L} = \text{P}(\text{OMe})_3$, allyl = $\text{C}_3\text{H}_4\text{Me-2}$] revealed the cations to be fluxional. At 30 °C, irradiation at δ 3.38 leads to a reduction in the intensity of the signal at δ 4.43 (Figure 1), clearly indicating exchange between the two *anti*-protons H_{a1} and H_{a2} . At –40 °C, however, no such exchange is observed (Figure 2).

That the *anti*-protons undergo slow exchange at 30 °C, without *syn-anti* interconversion, shows that the fluxional process involves slow allyl rotation. A similar process occurs for $[\text{FeX}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{or NCO}$)⁴ but the low-temperature limiting spectra for these species reveal the presence of two isomers (*exo* and *endo*) in contrast to the single isomer for (1).

The reactions of complexes (1) with nucleophiles are dominated by the loss of the allyl ligand. Thus, for example, (1; $\text{L} = \text{PPh}_3$, allyl = C_3H_5) reacts with chloride ion to give the paramagnetic complex $[\text{FeCl}(\text{PPh}_3)(\text{NO})_2]$ [$\tilde{\nu}(\text{NO}) = 1787$ and 1728 cm^{-1} , $g_{\text{av.}} = 2.034$, $A_p = 50\text{ G}$; cf. ref. 5, $\tilde{\nu}(\text{NO}) = 1789$ and 1731 cm^{-1} , $g_{\text{av.}} = 2.0362$, $A_p = 52.1\text{ G}$] and [1; $\text{L} = \text{P}(\text{OMe})_3$ or PPh_3] reacts with L to give $[\text{FeL}_2(\text{NO})_2]$ [$\text{L} = \text{P}(\text{OMe})_3$ or PPh_3].⁶ The fate of the allyl group in these reactions has not been determined. However, of considerably more synthetic importance is the preliminary observation⁷ that complexes (1) undergo allyl-transfer reactions with electron-rich organometallics, resulting in C–C bond coupling. Thus, for example, the addition of [1; $\text{L} = \text{P}(\text{OMe})_3$, allyl = $\text{C}_3\text{H}_4\text{Me-2}$] to $[\text{Ru}(\text{CO})_2(\text{PPh}_3)(\eta^4\text{-cot})]$ (cot = cyclo-octatetraene), followed by deprotonation of the product, yields the allyl-substituted derivative $[\text{Ru}(\text{CO})_2(\text{PPh}_3)(\eta^4\text{-C}_8\text{H}_7\text{R})]$ ($\text{R} = \text{C}_3\text{H}_4\text{Me-2}$).

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. The compounds $[\text{Fe}(\text{CO})\text{L}(\text{NO})(\eta^3\text{-allyl})]$ [$\text{L} = \text{PPh}_3, \text{P}(\text{OMe})_3, \text{or P}(\text{OPh})_3$; allyl = $\text{C}_3\text{H}_5, \text{C}_3\text{H}_4\text{Me-1}, \text{or C}_3\text{H}_4\text{Me-2}$] were prepared by the published method;⁸ the salt $[\text{NO}][\text{PF}_6]$ was purchased from Fluorochem Ltd., Glossop, Derbyshire.

Infrared spectra were recorded on a Perkin-Elmer PE 257 spectrometer. Proton n.m.r. spectra were recorded on a JEOL

† Non-S.I. unit employed: $\text{G} = 10^{-4}\text{ T}$.

Table 1. Analytical and i.r. spectral data for $[\text{FeL}(\text{NO})_2(\eta^3\text{-allyl})][\text{PF}_6]$ (1)

| L | Allyl | Yield (%) | Analysis ^a | | | $\bar{\nu}(\text{NO})^b/\text{cm}^{-1}$ |
|--------------------------|-----------------------------------|-----------|-----------------------|-----------|-----------|---|
| | | | C | H | N | |
| $\text{P}(\text{OMe})_3$ | C_3H_5 | 78 | 16.9 (16.9) | 3.4 (3.3) | 6.4 (6.6) | 1 853, 1 801 |
| $\text{P}(\text{OMe})_3$ | $\text{C}_3\text{H}_4\text{Me-1}$ | 71 | 19.1 (19.1) | 3.8 (3.6) | 6.1 (6.4) | 1 843, 1 794 |
| $\text{P}(\text{OMe})_3$ | $\text{C}_3\text{H}_4\text{Me-2}$ | 70 | 19.4 (19.1) | 3.9 (3.6) | 6.3 (6.4) | 1 851, 1 798 |
| $\text{P}(\text{OPh})_3$ | C_3H_5 | 57 | 41.1 (41.2) | 3.4 (3.3) | 4.7 (4.6) | 1 865, 1 813 |
| $\text{P}(\text{OPh})_3$ | $\text{C}_3\text{H}_4\text{Me-2}$ | 64 | 42.2 (42.2) | 3.4 (3.5) | 4.5 (4.5) | 1 858, 1 807 |
| PPh_3 | C_3H_5 | 59 | — | — | — | 1 842, 1 792 |
| PPh_3 | $\text{C}_3\text{H}_4\text{Me-1}$ | 63 | — | — | — | 1 833, 1 785 |
| PPh_3 | $\text{C}_3\text{H}_4\text{Me-2}$ | 68 | — | — | — | 1 839, 1 789 |

^a Calculated values are in parentheses. ^b In CH_2Cl_2 .

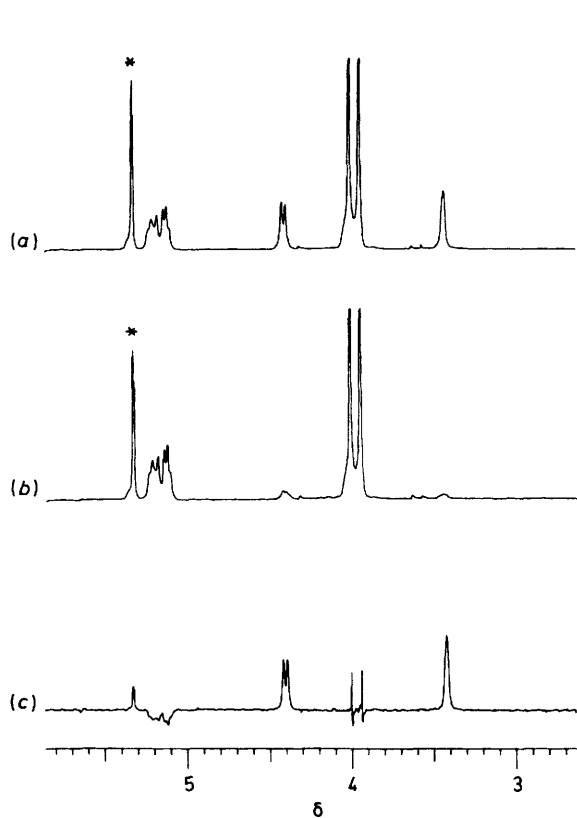


Figure 1. The ^1H n.m.r. spectrum of $[\text{Fe}\{\text{P}(\text{OMe})_3\}(\text{NO})_2(\eta^3\text{-C}_3\text{H}_4\text{Me-2})]^+$ at 30°C (a), with saturation at δ 3.38 (b), and spectrum (a) minus spectrum (b) [(c)]. The asterisks indicate peaks due to CD_2Cl_2

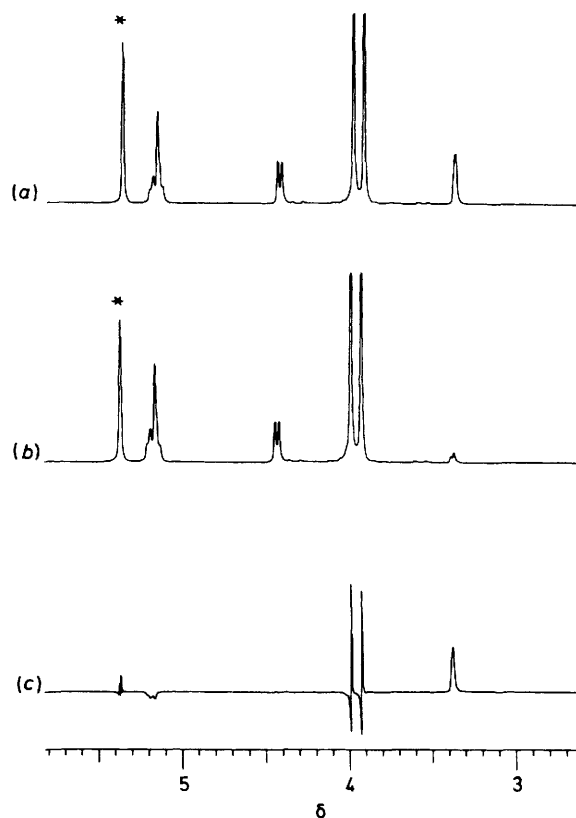


Figure 2. The ^1H n.m.r. spectrum of $[\text{Fe}\{\text{P}(\text{OMe})_3\}(\text{NO})_2(\eta^3\text{-C}_3\text{H}_4\text{Me-2})]^+$ at -40°C (a), with saturation at δ 3.38 (b), and spectrum (a) minus spectrum (b) [(c)]. Other details as in Figure 1

PS 100 or FX 200 instrument, ^{13}C n.m.r. spectra on the FX 200 instrument.

Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

(η -Allyl)dinitrosyl(trimethyl phosphite)iron Hexafluorophosphate, $[\text{Fe}\{\text{P}(\text{OMe})_3\}(\text{NO})_2(\eta^3\text{-C}_3\text{H}_5)][\text{PF}_6]$.—To a stirred solution of $[\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}(\text{NO})(\eta^3\text{-C}_3\text{H}_5)]$ (1.75 g, 6.27 mmol) in CH_2Cl_2 (90 cm^3) was added solid $[\text{NO}][\text{PF}_6]$ (1.05 g, 6.0 mmol). After 10 min the pale orange solution was filtered, and addition of diethyl ether (200 cm^3) gave the product as

orange crystals, yield 2.08 g (78%). The complex may be recrystallised from CH_2Cl_2 -diethyl ether if necessary.

The complexes $[\text{FeL}(\text{NO})_2(\eta^3\text{-allyl})][\text{PF}_6]$ [$\text{L} = \text{P}(\text{OPh})_3$, allyl = C_3H_5 or $\text{C}_3\text{H}_4\text{Me-2}$; $\text{L} = \text{P}(\text{OMe})_3$, allyl = $\text{C}_3\text{H}_4\text{Me-1}$ or -2 ; $\text{L} = \text{PPh}_3$, allyl = C_3H_5 , $\text{C}_3\text{H}_4\text{Me-1}$, or $\text{C}_3\text{H}_4\text{Me-2}$] were prepared similarly. All dissolve in CH_2Cl_2 to give air-sensitive solutions.

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Table 2. Proton and ^{13}C n.m.r. spectral data for $[\text{FeL}(\text{NO})_2(\eta^3\text{-allyl})][\text{PF}_6]^a$

| L | Allyl | ^1H (δ) | $^{13}\text{C}^b$ (p.p.m.) |
|---------------------|---|---|---|
| P(OMe) ₃ | C ₃ H ₅ | 3.46 [1 H, d, $J(\text{H}_a, \text{H}_c)$ 15, H _a], 3.93 [9 H, d, $J(\text{MeP})$ 12, P(OMe) ₃], 4.45 [1 H, dd, $J(\text{H}_a, \text{H}_c)$ 14, $J(\text{H}_a, \text{P})$ 4.5, H _a], 5.26 [2 H, m, H _b], 5.54 [1 H, spt, $J(\text{H}_a, \text{H}_c)$ 15, $J(\text{H}_a, \text{H}_c)$ 14, $J(\text{H}_b, \text{H}_c)$ 9, $J(\text{H}_c, \text{P})$ 13, H _c] ^{c,d} | 55.4 [d, $J(\text{CP})$ 4.5, P(OMe) ₃], 73.1 [d, $J(\text{C}^2\text{P})$ 5, C ²], 81.4 (C ¹), 111.4 (C ³) |
| | C ₃ H ₄ Me-1 | 2.40 [3 H, t, $J(\text{H}_b, \text{Me})$ 5, $J(\text{MeP})$ 5, Me], 3.23 [1 H, d, br, $J(\text{H}_a, \text{H}_c)$ 13, H _a], 3.91 [9 H, d, $J(\text{MeP})$ 12, P(OMe) ₃], 5.02 (1 H, m, H _b), 5.46 (2 H, m, H _b , H _c] ^{c,d} | 21.7 (Me), 55.2 [d, $J(\text{CP})$ 6, P(OMe) ₃], 75.8 [d, $J(\text{C}^1\text{P})$ 4.5, C ¹], 100.1 [d, $J(\text{C}^2\text{P})$ 9, C ²], 110.1 (C ³) |
| | C ₃ H ₄ Me-2 | 1.87 (3 H, s, Me), 3.38 (1 H, s, br, H _a), 3.95 [9 H, d, $J(\text{MeP})$ 12, P(OMe) ₃], 4.43 [1 H, d, $J(\text{H}_a, \text{P})$ 5, H _a], 5.20 (2 H, m, H _b] ^{c,e} | 22.9 (Me), 55.5 [d, $J(\text{CP})$ 6, P(OMe) ₃], 73.3 [d, $J(\text{C}^2\text{P})$ 9, C ²], 82.0 [d, $J(\text{C}^1\text{P})$ 6, C ¹], 130.4 (C ³) |
| P(OPh) ₃ | C ₃ H ₅ | 3.45 (1 H, s, br, H _a), 4.30 (1 H, s, br, H _a), 5.16 (3 H, m, br, H _b , H _c), 7.3 [15 H, m, P(OPh) ₃] ^{g,h} | |
| | | 3.25 [1 H, d, $J(\text{H}_a, \text{H}_c)$ 12, H _a], 4.20 (1 H, d, $J(\text{H}_a, \text{H}_c)$ 12, H _a], 4.98 (3 H, m, H _b , H _c), 7.3 [15 H, m, P(OPh) ₃] ^{g,i} | |
| | C ₃ H ₄ Me-2 | 1.44 (3 H, s, Me), 3.24 (1 H, s, br, H _a), 4.31 (1 H, s, br, H _a), 4.99 (1 H, s, br, H _b), 5.20 (1 H, s, br, H _b), 7.3 [15 H, m, P(OPh) ₃] ^{g,h} | |
| | 1.30 (3 H, s, Me), 3.20 (1 H, s, H _a), 4.35 (1 H, s, H _a), 4.95 [1 H, d, $J(\text{H}_b, \text{H}_c)$ 3, H _b], 5.20 [1 H, d, $J(\text{H}_b, \text{H}_c)$ 3, H _b], 7.3 [15 H, m, P(OPh) ₃] ^{g,i} | 21.7 [q, $J(\text{Me})$ 130, Me], 55.2 [m, P(OMe) ₃], 75.8 (t, br, $J(\text{C}^1\text{H}_a)$, $J(\text{C}^1\text{H}_b)$) 156, C ¹], 100.1 [d, br, $J(\text{C}^2\text{H}_b)$] 169, C ²], 110.1 [d, $J(\text{C}^3\text{H}_c)$] 162, C ³] ^f | |

^a In CD₂Cl₂, J in Hz; assignments refer to structure (A). ^b At 50 MHz and at -40°C . ^c 200-MHz Spectrum. ^d At -10°C . ^e At -40°C . ^f Proton-coupled spectrum. ^g Phosphorus-decoupled 100-MHz spectrum. ^h Room temperature. ⁱ At -50°C .

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