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Preliminary communication

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# Cationic Allyldinitrosyl Complexes of Iron

by Paul K. Baker and Neil G. Connelly*

(Department of Inorganic Chemistry, University of Bristol, Bristol
BS8 1TS)

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Summary The nitrosonium ion, $[NO]^+$, and $[Fe(CO)L(NO)(\eta^3\text{-allyl})]$ $[L = PPh_3$ or $P(OMe)_3$, allyl $= C_3H_5$, 1-$MeC_3H_4$, or 2-$MeC_3H_4]$ react to give the fluxional cation $[FeL(NO)_2(\eta^3\text{-allyl})]^+$, which undergoes allyl displacement with nucleophiles.

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The $Fe(NO)_2$ group is currently under investigation as a catalyst for the cyclodimerisation of dienes[1], and it has been proposed[2] that allyldinitrosyl intermediates are involved in cyclooligomerisation reactions catalysed by $[Fe(CO)_2(NO)_2]$. Until now only one allyldinitrosyl complex of iron, $[Cl_2Sn\{Fe(NO)_2(\eta^3\text{-}C_3H_5)\}_2]$ has been fully characterised and it is noteworthy that this species is also catalytically active.[3] We now report the synthesis of the cationic complexes $[FeL(NO)_2(\eta^3\text{-allyl})]^+$, and preliminary studies of their fluxionality and reactivity.

Equimolar quantities of $[NO][PF_6]$ and $[Fe(CO)L(NO)(\eta^3\text{-allyl})]$ $[L = PPh_3$ or $P(OMe)_3$, allyl $= C_3H_5$, 1-$MeC_3H_4$, or 2-$MeC_3H_4]^4$ react in $CH_2Cl_2$ to give the orange, crystalline salts $[FeL(NO)_2(\eta^3\text{-allyl})][PF_6]$. The phosphite complexes are stable in the solid state when stored under nitrogen and have been fully characterised by element analysis (C, H and N) and by i.r. and $^1H$ n.m.r. spectroscopy (Table). The phosphine

I.r. and $^1$H n.m.r. Data for $[FeL(NO)_2(\eta^3\text{-allyl})][PF_6]$

| L | allyl | $\bar{\nu}$(NO) cm$^{-1}$ [a] | $\tau$[b] | | | |
|---|---|---|---|---|---|---|
| | | | Ha | Hb | Hc | Methyl Protons |
| $P(OMe)_3$ | $C_3H_5$ | 1 853, 1 801 | 6.48 {1H, d, $J_{HaHc}$ 14 Hz}<br>5.58 {1H, d, $J_{HaHc}$ 13 Hz} | 4.74 (2H, m) | 4.52 (1H, m) | 6.06 {9H, s, $J_{PH}$ 14 Hz[c], $P(OMe)_3$} |
| $P(OMe)_3$ | 1-$MeC_3H_4$[d] | 1 843, 1 794 | 6.78 {1H, brd.d, $J_{HaHc}$ 12 Hz} | 4.96 (1H, m)<br>4.50 (1H, m)[e] | 4.50 (1H, m)[e] | 6.08 {9H, s, $J_{PH}$ 13 Hz[c], $P(OMe)_3$}<br>7.62 {3H, d, $J_{H_{Me}H_b}$ 5 Hz}[f] |
| $P(OMe)_3$ | 2-$MeC_3H_4$ | 1 851, 1 798 | 6.63 (1H, s)<br>5.60 (1H, s) | 4.86 (2H, brd.s) | - | 6.06 {9H, s, $J_{PH}$ 12 Hz[c], $P(OMe)_3$}<br>8.16 (3H, s) |
| $PPh_3$ | $C_3H_5$ | 1 842, 1 792 | | | | |
| $PPh_3$ | 1-$MeC_3H_4$ | 1 833, 1 785 | - | - | - | - |
| $PPh_3$ | 2-$MeC_3H_4$ | 1 839, 1 789 | | | | |

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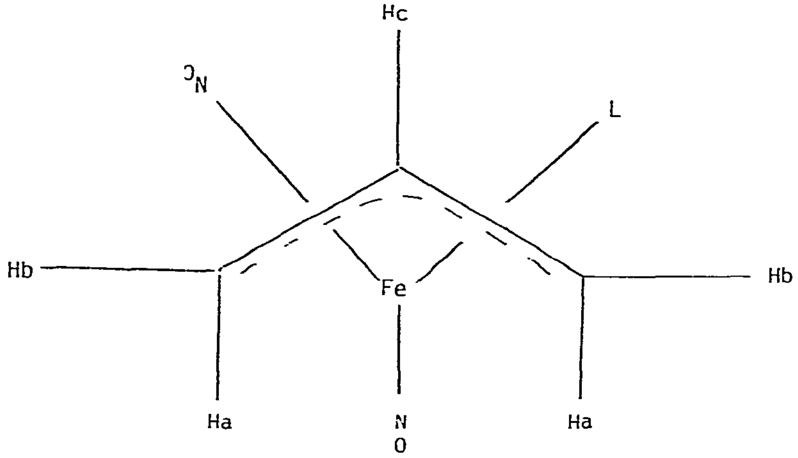
[a] In $CH_2Cl_2$. [b] $^{31}$P-decoupled, in $CD_2Cl_2$ at 0°C, numbering as in Figure. [c] $J_{PH}$ from $^{31}$P-coupled spectrum. [d] Only *anti*-methyl isomer present. [e] Signals coincident. [f] Signal is triplet in $^{31}$P-coupled spectrum, $J_{PH}$ 12 Hz.

analogues are much less stable and no n.m.r. spectra have been recorded.

The variable temperature (-30 to +25°C) $^{31}$P-decoupled $^{1}$H n.m.r. spectra of $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})][PF_6]$ show that the cations are fluxional. Below $0^oC$ the spectra are as expected for a static structure in which the $\eta^3$-allyl ligand is bonded to an unsymmetric $Fe\{P(OMe)_3\}(NO)_2$ group; the anti-protons $H_a$ (Figure) are inequivalent as are the syn-protons $H_b$. As the temperature is raised allyl rotation results in the broadening and coalescence of, for example, the two singlets ($\tau$ = 5.60 and 6.63) due to the anti-protons of the $2\text{-MeC}_3H_4$ ligand. Details of the fluxional behaviour of $[FeL(NO)_2(\eta^3\text{-allyl})]^+$ and of the isoelectronic carbonyls $[Fe(CO)L(NO)(\eta^3\text{-allyl})]^4$ will be presented at a later date.

The chemistry of $[FeL(NO)_2(\eta^3\text{-allyl})][PF_6]$ is dominated by allyl displacement. For example, hydride ion, sodium amalgam, and L each afford $[FeL_2(NO)_2]$, and chloride ion yields paramagnetic $[FeClL(NO)_2]^5$ in an unusual electron-transfer reaction.



Figure

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