Synthesis of tetrasubstituted derivatives of $[Fe_3(CO)_{12}]$

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The treatment of $[Fe_3(CO)_{10}L^1L^2]$ [L^1, L^2 = CO, $P(OMe)_3$, $P(OCH_2)_3CMe$] with $CNBu^t$ in the presence of Me_3NO yields the tetrasubstituted derivatives, $[Fe_3(CO)_8(CNBu^t)_4]$, $[Fe_3(CO)_8(CNBu^t)_3\{P(OMe)_3\}]$, $[Fe_3(CO)_8(CNBu^t{}_3)\{P(OCH_2)_3CMe\}]$, $[Fe_3(CO)_8(CNBu^t{}_3)_2\{P(OCH_2)_3CMe\}_2]$, $[Fe_3(CO)_8(CNBu^t)_2\{P(OCH_2)_3CMe\}\{P(OMe)_3\}]$ and $[Fe_3(CO)_8(CNBu^t{}_3)_2\{P(OMe)_3\}_2]$; the compounds were characterised by analysis, mass spectrometry, IR, and (in part) ^1H and ^{31}P NMR spectroscopy.

Highly substituted derivatives of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ are well known, with crystal structures having been determined for $[Os_3(CO)_8\{P(OMe)_3\}_2(\mu\text{-dppm})]$,[1] $[Os_3(CO)_8\{P(OMe)_3\}_2(PPh_3)_2]$,[1] $[Ru_3(\mu\text{-}CO)_2(CO)_6\{PPh(OMe)_2\}_4]$,[2] $[Ru_3(CO)_8[\{(MeO)_2P\}_2NEt]_2]$,[3] $[Ru_3(CO)_8\{AsMe_2C{=}C(AsMe_2)CF_2CF_2\}_2]$,[4] $[Ru_3(CO)_8\{P(OPh)_3\}_4]$,[5] $[Ru_3(CO)_8\{P(OMe)_3\}_4]$,[5] $[Ru_3(\mu\text{-}CO)_3(CO)_5\{P(OEt)_3\}_4]$,[5] and $[Ru_3(CO)_{10}(dpam)]$.[6] In addition, hexasubstituted derivatives are known *i.e.* $[Ru_3(CO)_6(dppm)_3]$[7,8] and $[Os_3(CO)_6\{P(OMe)_3\}_6]$.[9]

In contrast, substitution of carbonyls in $[Fe_3(CO)_{12}]$ is only known as far as the tris derivatives, with crystal structures having been determined for $[Fe_3(CO)_9(PMe_2Ph)_3]$,[10] $[Fe_3(CO)_9\{P(OMe)_3\}_3]$,[11] and $[Fe_3(CO)_9\{P(OPr^i)_3\}_3]$.[11] $[Fe_3(CO)_{12}]$ readily fragments on substitution to give mainly monomeric compounds.[12] Recently it has been shown that substitution of $[Fe_3(CO)_{12}]$ proceeds smoothly when Me_3NO is used as the reagent.[13] We have been using this procedure to synthesise a range of derivatives of $[Fe_3(CO)_{12}]$. When $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$ is reacted with $CNBu^t$ in CH_2Cl_2 in the presence of Me_3NO, in addition to the expected product, $[Fe_3(CNBu^t)(CO)_9\{P(OMe)_3\}_2]$, a second green band due to $[Fe_3(CNBu^t)_2(CO)_8\{P(OMe)_3\}_2]$ was observed on the silica gel column. The production of this second derivative was optimised by using *ca.* 10 mol of $CNBu^t$ and *ca.* 20 mol of Me_3NO per mol of $[Fe_3(CO)_{10}\{P(OMe)_3\}_2]$ in CH_2Cl_2 and allowing the reaction to procede for 2–3 d at room temp. under nitrogen. Subsequent chromatography on silica gel using CH_2Cl_2 as eluent yielded the product, $[Fe_3(CNBu^t)_2(CO)_8\{P(OMe)_3\}_2]$ in 5% yield. The compound was characterised by ^1H and ^{31}P NMR and IR spectroscopy, mass spectrometry and elemental analysis.[14] Attempts to grow suitable crystals for X-ray diffraction have failed.

The same procedure was used to synthesise $[Fe_3(CNBu^t)_2(CO)_8\{P(OCH_2)_3CMe\}_2]$, $[Fe_3(CNBu^t)_2(CO)_8\{P(OMe)_3\}\{P(OCH_2)_3CMe\}]$, $[Fe_3(CNBu^t)_3(CO)_8\{P(OMe)_3\}]$, $[Fe_3(CNBu^t)_3(CO)_8\{P(OCH_2)_3CMe\}]$ and $[Fe_3(CNBu^t)_4(CO)_8]$ except in that an alumina column was used for $[Fe_3(CNBu^t)_3\{P(OMe)_3\}]$ and $[Fe_3(CNBu^t)_4(CO)_8]$. Yields are low varying between 5 and 15%, with the highest yield being obtained for $[Fe_3(CNBu^t)_3(CO)_8\{P(OCH_2)_3CMe\}]$. The compounds decompose quite readily in solution and this prevented the observation of ^{13}C NMR spectra. All the compounds were characterized using elemental analysis, IR spectroscopy and mass spectrometry.† In solution they slowly decompose to give significant concentrations of the monomeric derivatives. This coupled with the exchange between stereoisomers made it difficult to obtain reliable NMR spectra.

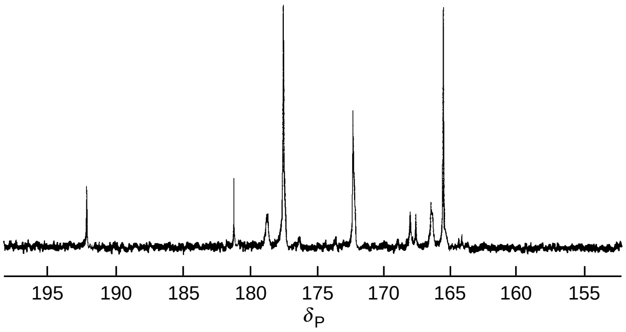
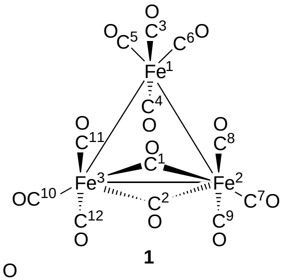


Fig. 1 The 162 MHz ^{31}P NMR spectrum of $[Fe_3(CNBu^t)_2(CO)_8\{P(OMe)_3\}_2]$ in $[^2H_8]$toluene at 223 K. Note that the signals at δ 181 and 192 are impurities.

In general, the ^{31}P NMR spectra were the most informative. For example for $[Fe_3(CNBu^t)_2(CO)_8\{P(OMe)_3\}_2]$, which in solution exists as a mixture of at least four isomers, the ^{31}P NMR spectrum] in $[^2H_8]$toluene at room temp. is broad, but at 223 K has seven ^{31}P NMR signals at δ 165.7, 166.4 (J 13 Hz), 167.7, 168.1, 172.3, 177.5 and 178.8 (J 13 Hz) in significant intensities for $[Fe_3(CNBu^t)_2(CO)_8\{P(OMe)_3\}_2]$, Fig. 1. By using signal intensity and the coupling constant, these signals form three pairs and one singlet in the ratio 1.00 : 0.30 : 0.30 : 0.14, the pairs being δ 177.5 and 165.7, δ 178.8 and 166.4 and δ 168.1 and 167.7. It has been previously shown that $P(OMe)_3$ on the unbridged iron is at higher frequency than when on a bridged iron, and when the $P(OMe)_3$ ligands are in a linear arrangement, P–Fe–Fe–P, then a $J(^{31}P^{31}P)$ of *ca.* 6–25 Hz is observed.‡

It is known that the concerted bridge-opening bridge-closing mechanism is far too rapid to stop even at −100 °C when phosphorus substitution is only in positions 6 and/or 10, numbering as in **1**.[15] The introduction of a $CNBu^t$ does slow the



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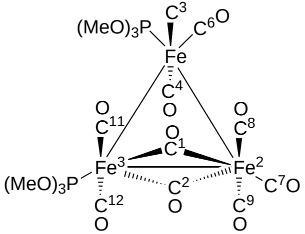

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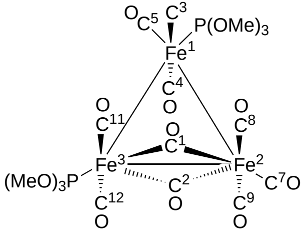

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rate of the concerted bridge-opening bridge-closing mechanism sufficiently to cause substantial broadening at −100 °C in $[Fe_3(CNBu^t)(CO)_{11}]$ or $[Fe_3(CNBu^t)(CO)_{10}\{P(OMe)_3\}]$.[16] It is also known that the $CNBu^t$ ligand has a preference for an axial site on the unbridged iron, Fe^1, in so far as the crystal structures of $[Fe_3(CNBu^t)(CO)_{11}]$,[17] $[Fe_3(CNBu^t)_2(CO)_{10}]$[18] and $[Fe_3(CNBu^t)(CO)_{10}\{P(OMe)_3\}]$[16] have an isonitrile in this position. In the case of $[Fe_3(CNBu^t)_2(CO)_{10}]$, the second $CNBu^t$ is also on the unbridged iron, Fe^1, but in the equatorial position.

The ^{31}P NMR signals at δ 177.5 and 165.7 do not show $J(^{31}P^{31}P)$ and arise from an isomer with a bent phosphorus ligand arrangement as in **2**. The ^{31}P NMR signal at δ 172.3 arises from the concerted bridge-opening bridge-closing mechanism averaging the $P(OMe)_3$ ligands. This is consistent with the phosphorus ligands being arranged as in **3** and one $CNBu^t$ ligand being substituted into the ligand set 3, 5, 4, 9, 8 and the other $CNBu^t$ ligand being substituted into the ligand set 1, 12, 11, 2, 7. The third most intense set of signals at δ 166.4 and 178.8, $J(^{31}P^{31}P)$ 13 Hz, arises from **3** with both $CNBu^t$ ligands in one ligand set, probably, 3, 5, 4, 9, 8.

There is less information available to assign the structures of the other compounds.

We wish to thank the University of Sheffield for financial support.

Footnotes and References

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† $[Fe_3(CNBu^t)_2(CO)_8\{P(OMe)_3\}_2]$. Anal. Calc. C, 35.76; H, 4.50; N, 3.48 for $C_{24}H_{36}Fe_3N_2O_{14}P_2$. Found: C, 35.71; H, 4.43; N, 3.33%. Mass spectrum: m/z 806 (M^+). IR (CH_2Cl_2): 2139m, 2014w, 1973s, 1956s, 1750w (br), 1753w cm^{-1}. ^1H NMR ($CD_3C_6D_5$): δ 1.20 (18 H), 3.33 (18 H). $[Fe_3(CNBu^t)_2(CO)_8\{P(OCH_2)_3CMe\}_2]$. Anal. Calc. C, 39.38; H, 4.25; N, 3.28 for $C_{28}H_{36}Fe_3N_2O_{14}P_2$. Found: C, 39.26; H, 4.21; N, 3.12%. Mass spectrum: m/z 854 (M^+). IR (CH_2Cl_2): 2145m, 2020w, 1981s, 1963s, 1762w (br) cm^{-1}. $[Fe_3(CNBu^t)_2(CO)_8\{P(OMe)_3\}\{P(OCH_2)_3CMe\}]$. Anal. Calc. C, 37.62; H, 4.37; N, 3.37 for $C_{26}H_{36}Fe_3N_2O_{14}P_2$. Found: C, 38.10; H, 4.45; N, 3.42%. Mass spectrum: m/z 830 (M^+). IR (CH_2Cl_2): 2142m, 2017w, 1976s, 1960s, 1751w (br) cm^{-1}. ^1H NMR ($CD_3C_6D_5$): $[Fe_3(CNBu^t)_2(CO)_8\{P(OMe)_3\}\{P(OCH_2)_3CMe\}]$ shows the integral of the overlapped signals at δ 3.3, which are due to methyl groups of $P(OMe)_3$ and methylene of $P(OCH_2)_3CMe$, and the overlapped signals around δ 1.20, which arise from the protons of $CNBu^t$ and methyl groups of $P(OCH_2)_3CMe$, is 15 : 21. $[Fe_3(CNBu^t)_3(CO)_8\{P(OMe)_3\}]$. Anal. Calc. C, 40.82; H, 4.74; N, 5.49 for $C_{26}H_{36}Fe_3N_3O_{11}P$. Found: C, 40.73; H, 4.88; N, 5.14%. Mass spectrum: m/z 765 (M^+). IR (CH_2Cl_2): 2162sh, 2132m, 2010w, 1971s, 1958s, cm^{-1}. ^1H NMR ($CD_3C_6D_5$): (room temp.), δ 1.20 (27 H), 3.48 (9 H). The ^{31}P NMR spectrum of $[Fe_3(CNBu^t)_3(CO)_8\{P(OMe)_3\}]$ in $[^2H_8]$toluene at 223 K shows there are at least seven signals at δ 164.1, 165.1, 165.9, 167.3, 169.0, 172.7 and 177.3 in the ratio 0.10 : 0.04 : 0.42 : 1.00 : 0.35 : 0.40 : 0.04, suggesting there are at least seven isomers in solution. $[Fe_3(CNBu^t)_3(CO)_8\{P(OCH_2)_3CMe\}]$. Anal. Calc. C, 42.62; H, 4.60; N, 5.32 for $C_{28}H_{36}Fe_3N_3O_{11}P$. Found: C, 42.27; H, 4.56; N, 5.22%. Mass spectrum: m/z 789 (M^+). IR (CH_2Cl_2): 2162(sh), 2136m, 2013w, 1975s, 1960s, 1800w (br), 1758w, (br) cm^{-1}. $[Fe_3(CNBu^t)_4(CO)_8]$. Anal. Calc. C, 46.44; H, 5.01; N, 7.74 for $C_{28}H_{36}Fe_3N_4O_8$. Found: C, 46.23; H, 4.92; N, 7.56%. Mass spectrum: m/z 724 (M^+). IR (CH_2Cl_2): 2135m, 2067w, 1998w, 1969s, 1956s, 1800w, (br) 1759w, (br) cm^{-1}.

‡ The ^{31}P NMR spectrum of $[Fe_3(CO)_9\{P(OMe)_3\}_3]$ in CD_2Cl_2 at −92 °C shows coupling between the signals at δ 171.5 and 163.8 which have previously been assigned to the $P(OMe)_3$ ligands on Fe^1 and Fe^3 respectively, see ref. 14.

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Received in Cambridge, UK, 18th August 1997; 7/06054H