ChemComm

Poly-carbon chemistry: reactions of the multi-site coordinated diyndiyl ligand in $\{Fe_2(CO)_6(\mu\text{-}PPh_2)\}_2(\mu\text{-}\eta^1,\eta^2:\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}C{-}C{\equiv}C)$ with the nucleophiles $P(OMe)_3$ and $NHEt_2$†

Paul J. Low,*[ab] Arthur J. Carty,*[ac] Konstantin A. Udachin[a] and Gary D. Enright[a]

[a] *Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A 0R6*

[b] *Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE. E-mail: p.j.low@durham.ac.uk*

[c] *Ottawa-Carleton Research Institute, Department of Chemistry, University of Ottawa, 1125 Colonel By Drive, Ottawa, Ontario, Canada, K1A 5B6*

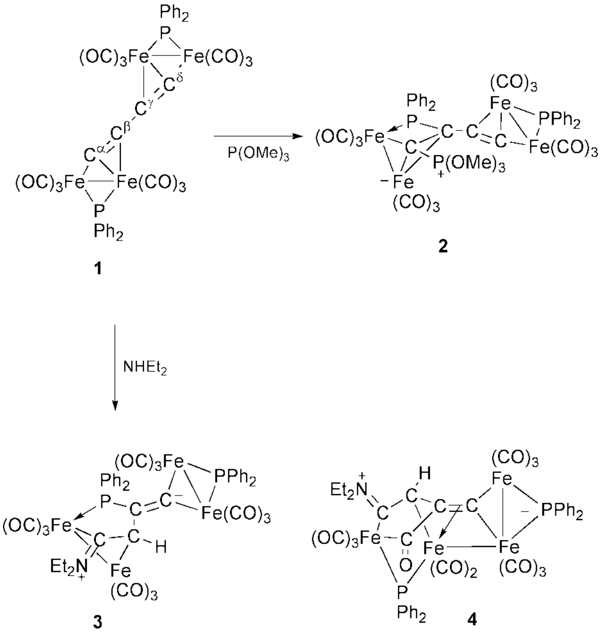
Received (in Cambridge, UK) 6th December 2000, Accepted 22nd January 2001
First published as an Advance Article on the web 9th February 2001

The diyndiyl complex $\{Fe_2(CO)_6(\mu\text{-}PPh_2)\}_2(\mu\text{-}C{\equiv}C{-}C{\equiv}C)$ reacts with $P(OMe)_3$ or $NHEt_2$ to give products derived from addition to C_α and facile P–C, N–C and/or C–C bond formation.

Transition metal diyndiyl (M–C≡C–C≡C–M) complexes are members of a rapidly expanding class of organometallic molecules bearing poly-unsaturated, all-carbon molecules as ligands. While the synthesis of compounds featuring polyynyl and polyyndiyl ligands has advanced rapidly,[1] the reactivity of these carbon-rich materials is relatively unexplored.[2] Herein we describe some remarkable reactions of the diyndiyl complex $\{Fe_2(CO)_6(\mu\text{-}PPh_2)\}_2(\mu\text{-}C_\alpha{\equiv}C_\beta{-}C_\gamma{\equiv}C_\delta)$ (**1**) with the nucleophiles $NHEt_2$ and $P(OMe)_3$.

The tetra-iron diyndiyl complex $\{Fe_2(CO)_6(\mu\text{-}PPh_2)\}_2(\mu\text{-}C_\alpha{\equiv}C_\beta{-}C_\gamma{\equiv}C_\delta$ (**1**), previously obtained in only very low yields from a two-step reaction,[3] may be conveniently obtained (35%) directly from the reaction of $Fe_3(CO)_{12}$ with $Ph_2PC{\equiv}CC{\equiv}CPPh_2$ in THF *via* a facile P–C (alkynyl) bond cleavage reaction. Treatment of **1** with an excess of $P(OMe)_3$ in benzene resulted in the formation of the dark red adduct **2** (Scheme 1, Fig. 1),[4,5]† together with the simple phosphite-substituted complexes $\{Fe_2(\mu\text{-}PPh_2)(CO)_5[P(OMe)_3]\}(\mu\text{-}C{\equiv}CC{\equiv}C)\{Fe_2(\mu\text{-}PPh_2)(CO)_5(L)\}$ [L = CO, $P(OMe)_3$]. Compound **2** is derived from addition of the phosphite reagent to only one ynyl functionality of the original butadiyndiyl ligand at C_α, followed by migration of the associated diphenylphosphido group to C_β and P–C bond formation to give a simple 2e-phosphine. This contrasts with the reactions of the analogous mono-acetylide complex $Fe_2(\mu\text{-}C{\equiv}CPh)(CO)_6(\mu\text{-}PPh_2)$ with $P(OR)_3$ (R = Me, Et, Bu^n) which gave $Fe_2(CO)_6\{C[P(OR)_3]CPh\}(\mu\text{-}PPh_2)$ quantitatively.[6] An examination of the molecular structure of the Et product suggests that C_β is sterically protected by both $P(OEt)_3$ and Ph groups, which probably hinders the migration of the PPh_2 moiety.[6]

While **1** failed to react with the bulky reagents dicyclohexylamine and diphenylamine (benzene, 80 °C), treatment of **1** with an excess of $NHEt_2$ (r.t., 2 d) resulted in the formation of purple **3** (Fig. 2) and red **4** (Fig. 3) in 19 and 33% yield respectively (Scheme 1).[4,5] Complex **3** contains two $Fe_2(CO)_6$ moieties bridged by an unusual 1-diethylamino-3-diphenylphosphinobuteneylidene ligand, obtained from 1,2-addition of the amine N–H bond across one acetylide moiety in **1**, with migration of a PPh_2 phosphino group to C_γ. The major product **4** is also derived from 1,2-addition of the amine to the carbon ligand, although in this case it is a carbonyl ligand rather than the PPh_2 group that has migrated from iron to C_γ yielding the five-membered metallacyclic ligand. The addition of the



Scheme 1 Reaction of **1** with $P(OMe)_3$ and $NHEt_2$.

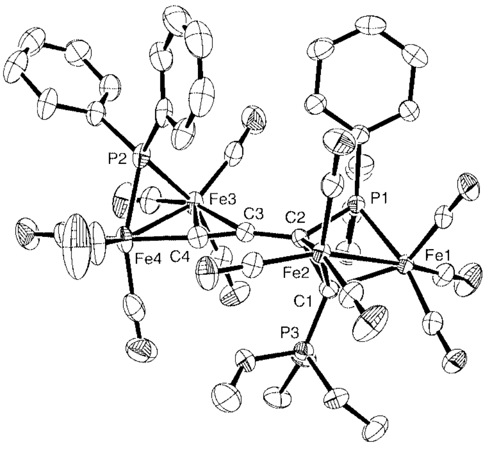


Fig. 1 ORTEP drawing of **2**. Selected bond lengths (Å) and angles (°): Fe(1)–Fe(2) 2.6033(4), Fe(3)–Fe(4) 2.5754(4), C(1)–C(2) 1.498(3), C(2)–C(3) 1.443(2), C(3)–C(4) 1.229(3), Fe(1)–C(1) 2.025(2), Fe(2)–C(1) 1.9457(2), Fe(2)–C(2) 2.072(2), Fe(1)–P(1) 2.2316(6), P(1)–C(2) 1.782(2), Fe(3)–C(3) 2.469(2), Fe(3)–C(4) 2.105(2), Fe(4)–C(4) 1.906(2), P(3)–C(1) 1.708(2); C(1)–C(2)–C(3) 126.5(1), C(2)–C(3)–C(4) 162.2(2), C(3)–C(4)–Fe(4) 171.5(2), Fe(1)–P(1)–C(2) 86.10(7).

---

† Electronic supplementary information (ESI) available: reaction details and spectroscopic data. See http://www.rsc.org/suppdata/cc/b0/b009797g/

DOI: 10.1039/b009797g

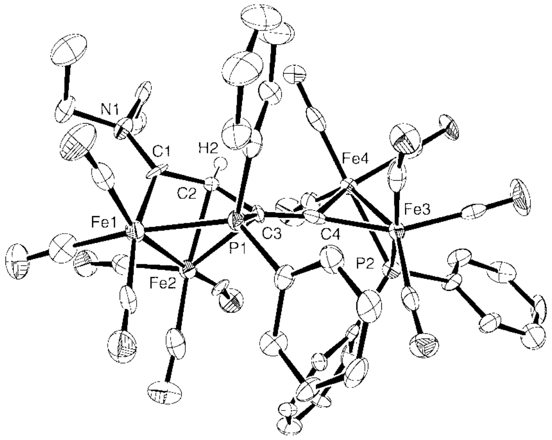


Fig. 2 Molecular structure of one molecule of **3**. Selected bond lengths (Å) and angles (°): Fe(1)–Fe(2) 2.665(2), Fe(3)–Fe(4) 2.540(2), Fe(1)–C(1) 2.020(9), Fe(1)–P(1) 2.233(3), N(1)–C(1) 1.33(1), P(1)–C(3) 1.813(9), Fe(2)–C(1) 2.458(9), Fe(2)–C(2) 2.033(9), Fe(2)–C(3) 2.212(9), Fe(3)–C(4) 1.95(1), Fe(4)–C(4) 1.933(9), C(1)–C(2) 1.43(1), C(2)–C(3) 1.46(1), C(3)–C(4) 1.40(1); Fe(1)–P(1)–C(3) 98.9(3), Fe(1)–C(1)–N(1) 127.4(7), N(1)–C(1)–C(2) 118.2(8), C(2)–C(3)–C(4) 121.4(8).

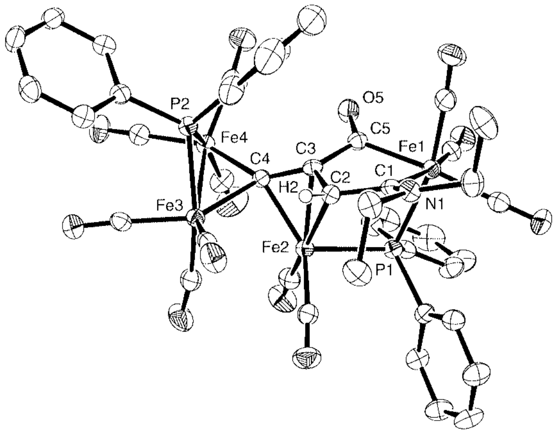


Fig. 3 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Fe(2)–Fe(3) 2.831(1), Fe(3)–Fe(4) 2.582(1), Fe(1)–P(1) 2.315(1), Fe(1)–C(1) 2.008(3), Fe(1)–C(5) 2.032(3), N(1)–C(1) 1.324(4), C(1)–C(2) 1.457(5), C(2)–C(3) 1.434(4), C(3)–C(4) 1.390(5), C(3)–C(5) 1.518(5), Fe(2)–C(2) 2.110(3), Fe(2)–C(3) 2.015(3), Fe(2)–C(4) 2.034(3), Fe(3)–C(4) 2.036(3), Fe(4)–C(4) 1.928(3); Fe(1)–P(1)–Fe(2) 106.14(4), Fe(1)–C(1)–N(1) 130.3(3), N(1)–C(1)–C(2) 117.8(3), C(1)–C(2)–C(3) 114.6(3), C(2)–C(3)–C(4) 119.9(3), C(2)–C(3)–C(5) 114.1(3), Fe(4)–C(4)–C(3) 140.6(2).

nucleophile is accompanied by significant rearrangement of the metal framework. The regiospecific 1,2-addition of $NHEt_2$ to C_α/C_β in the diyndiyl complex **1** is unusual in that the corresponding mono-ynyl iron complexes give β-addition products exclusively,[7] while the related ruthenium diynyl compounds give products derived from 1,4-addition of an N–H bond.[8]

Further studies of these remarkable rearrangements, which proceed with total atom conservation and demonstrate facile N–C, P–C and C–C bond formation involving the diyndiyl ligand, are in progress.

We are grateful to the National Research Council of Canada and the Natural Sciences and Engineering Research Council of Canada for financial support of this work. We thank Dr H. Puschmann for crystallographic assistance. P. J. L. held an NRC/NSERC Canadian Government Laboratories Visiting Fellowship.

Notes andreferences

1 R. Dembinski, T. Bartik, B. Bartik, M. Jaeger and J. A. Gladysz, *J. Am. Chem. Soc.*, 2000, **122**, 810; F. Paul and C. Lapinte, *Coord. Chem. Rev.*, 1998, **178–180**, 431; M. I. Bruce, M. Ke, P. J. Low, B. W. Skelton and A. H. White, *Organometallics*, 1998, **17**, 3539; M. Akita, M.-C. Chung, A. Sakurai, S. Sugimoto, M. Terada, M. Tanaka and Y. Moro-oka, *Organometallics*, 1997, **16**, 4882; P. Blenkiron, J. F. Corrigan, D. Pilette, N. J. Taylor and A. J. Carty, *Can. J. Chem.*, 1996, **74**, 2349 and references therein.

2 M. I. Bruce, B. C. Hall, B. D. Kelly, P. J. Low, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1999, 3719; M. I. Bruce, P. J. Low, N. N. Zaitseva, S. Kahal, J.-F. Halet, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2000, 2939; M. Akita, A. Sakurai and Y. Moro-oka, *Chem. Commun.*, 1999, 101. R. Dembinski, T. Lis, S. Szafert, C. L. Mayne, T. Bartik and J. A. Gladysz, *J. Organomet. Chem.*, 1999, **578**, 229; M. Akita, M.-C. Chung, M. Terada, M. Miyauti, M. Tanaka and Y. Moro-oka, *J. Organomet. Chem.*, 1998, **565**, 49; F. Leroux, R. Stumpf and H. Fischer, *Eur. J. Inorg. Chem.*, 1998, 1225; P. Blenkiron, G. D. Enright, N. J. Taylor and A. J. Carty, *Organometallics*, 1996, **15**, 2855.

3 C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1993, **450**, C9.

4 *Selected spectroscopic data* for **2**: IR (cyclohexane, ν/cm^{-1}): 2061m, 2044vs, 2020s, 2003s, 1997s, 1985s, 1980s, 1958m, 1944w. FAB-MS: *m*/*z* 1102 [M]$^+$, 1046–794, [M − *n*CO]$^+$ (*n* = 1–11). For **3**: IR (cyclohexane, ν/cm^{-1}): 2058m, 2040vs, 2017s, 2008s, 1988sh, 1984s, 1968s, 1959m, 1943m. FAB-MS: *m*/*z* 1023–715 [M − *n*CO]$^+$ (*n* = 1–12). For **4**: IR (CH_2Cl_2, ν/cm^{-1}) 2069m, 2047vs, 2011vs, 1998m, 1987sh, 1965m, 1954sh, 1936sh. FAB-MS: *m*/*z* 968 [M − 3CO + H]$^+$, 912 [M − 5CO + H]$^+$, 854 [M − 7CO]$^+$. Satisfactory microanalytical data were obtained for all complexes reported.

5 X-Ray data were collected on a Siemens SMART CCD diffractometer [graphite monochromatised Mo-Kα radiation, λ = 0.71070 Å, T = 173(2) K] and ω-scan frames and structures solved using the SHELXTL suite of programs. Refinement on F^2 by full-matrix least squares techniques. *Crystal data* for **2**: $Fe_4P_3O_{15}C_{43}H_{29}\cdot 0.7CH_2Cl_2$, M = 1101.97, triclinic, space group $P\bar{1}$, a = 10.9884(5), b = 11.1706(5), c = 22.0560(10) Å, α = 81.65(1), β = 75.71(1), γ = 61.36(1)°, V = 2301.4(2) Å^3, Z = 2, μ = 1.407 mm^{-1}. 20767 reflections measured, 8085 unique (R_{int} = 0.0773) which were used in all calculations. $wR2$ = 0.1243 (all data). For **3**: $Fe_4NO_{12}P_2C_{44}H_{31}$, M = 1051.04, monoclinic, space group $P2_1/c$, a = 39.793(4), b = 11.639(1), c = 19.552(2) Å, β = 102.08(1)°, V = 8855(1) Å^3, Z = 4, μ = 1.577 mm^{-1}. 33404 reflections measured, 10058 unique (R_{int} = 0.1178), $wR2$ = 0.1549 (all data). For **4**: $Fe_4NO_{12}P_2C_{44}H_{31}$, M = 1051.04, monoclinic, space group $P2_1/n$, a = 14.404(1), b = 21.879(1), c = 14.448(1) Å, β = 105.52(5)°, V = 4387.2(5) Å^3, Z = 4, μ = 1.433 mm^{-1}. 37566 reflections measured, 10107 unique (R_{int} = 0.0722), $wR2$ = 0.1030 (all data). CCDC reference numbers 155050–155052. See http://www.rsc.org/suppdata/cc/b0/b009797g/ for crystallographic data in .cif or other electronic format.

6 Y. S. Wong, H. N. Paik, P. C. Chieh and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1975, 309.

7 A. A. Cherkas, L. H. Randall, N. J. Taylor, G. N. Mott, J. E. Yule, J. L. Guinmant and A. J. Carty, *Organometallics*, 1990, **9**, 1677.

8 P. Blenkiron, D. Pilette, J. F. Corrigan, N. J. Taylor and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1995, 2165.