Dalton Communications

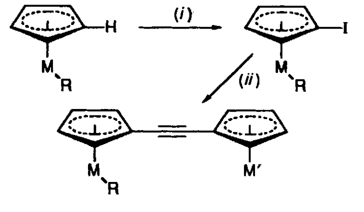
An Unprecedented Palladium-catalysed Carbon–Metal Bond Formation

Claudio Lo Sterzo
Centro C.N.R. di Studio sui Meccanismi di Reazione, c/o Dipartimento di Chimica, Universita' 'La Sapienza P. le A. Moro, 5-00185 Roma, Italy

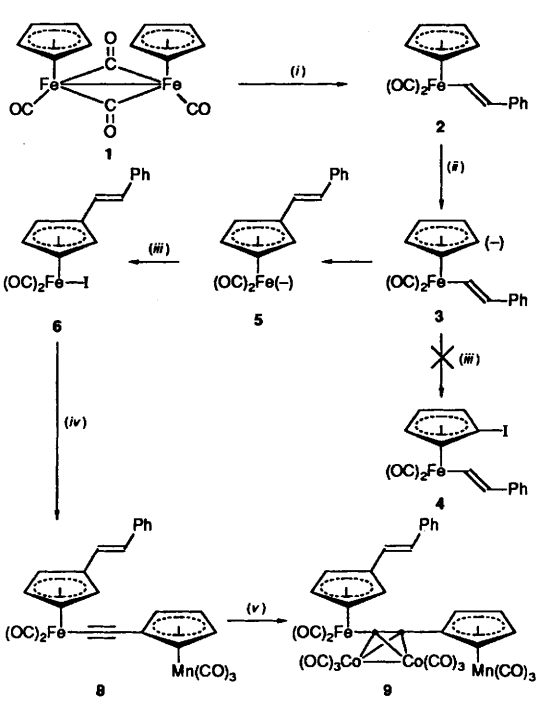
The reaction of $[Fe(\eta^5-C_5H_4R)(CO)_2I]$ (R = styryl) with $[Mn(\eta^5-C_5H_4C{\equiv}CSnMe_3)(CO)_3]$ in dimethylformamide in the presence of catalytic amounts (5%) of $[PdCl_2(MeCN)_2]$ produces $[(OC)_2(\eta^5-RC_5H_4)Fe{-}C{\equiv}C{-}(\eta^5-C_5H_4)Mn(CO)_3]$ in good yield; the crystal structure of the tetrahedral pyramidal adduct formed by reaction of this coupled product with $[Co_2(CO)_8]$ has been determined.

The ability of palladium to catalyse carbon–carbon bond formation with a wide variety of coupling partners is well documented.[1] Under uniquely mild conditions, organostannanes and a variety of other organometallic nucleophiles [2] have been coupled with organic electrophiles, in the presence of palladium, forming a wide variety of structures. The preparation of a number of bis(cyclopentadienyl)-framed polymetallic complexes assembled in a variety of structures *via* palladium-catalysed carbon–carbon coupling reactions was recently reported.[3] However, palladium-catalysed formation of other type of bonds is less known.

In this communication the unprecedented palladium-catalysed carbon–metal bond formation between $[Fe(\eta^5-C_5H_4R)(CO)_2I]$ and an alkynyltin compound is reported. In the course of my studies, directed toward the modification of bis(cyclopentadienyl)acetylene-framed polymetallic complexes, I was interested in the preparation of structures bearing a sterically demanding group on one metal (Scheme 1) in order to observe the effect of bulky ancillary ligands upon the reciprocal orientation of the metal centres in the solid state.[3d] Thus the complex $[Fe(\eta^5-C_5H_5)(CO)_2\{(E){-}CH{=}CHPh\}]$ **2** * was treated with $LiBu^s$ and 1,2-diiodoethane in order to obtain the corresponding iodocyclopentadienyl derivative **4**.[3a] Unexpectedly, treatment of the substrate with the base induced a shift of the styryl group from the iron to the ring, and subsequent quenching with iodine generated the iodoiron compound **6** instead of the iodocyclopentadienyl complex **4** (Scheme 2). This type of base-induced metal-to-cyclopentadienyl shift has already been observed[4] and extensively investigated[5] for a number of cyclopentadienylmetal derivatives, and it is supposed that a similar process occurs in the present reaction. Since **4** and **6** are isomers the rearrangement which had occurred remained undiscovered on the basis of elemental analysis and spectroscopic data alone. The product was then used for coupling with the tin acetylide **7** [3b] in the presence of a catalytic amount of palladium. The product was recovered in almost quantitative yield, and then treated with $[Co_2(CO)_8]$. Only a crystal structure determination carried out on complex **9** revealed the real synthetic pathway. Fig. 1 shows the molecular structure of the tetrametallic complex. The styryl group is unequivocally bonded to the cyclopentadienyl ring, resulting from the metal-to-cyclopentadienyl shift from **3** to **5**, and the alkyne moiety (masked by the dicobalt adduct) is linked to the iron atom.



Scheme 1 (*i*) Base, ICH_2CH_2I; (*ii*) $[M'(\eta^5-C_5H_4C{\equiv}CSnR'_3)]$, $[PdCl_2(MeCN)_2]$



Scheme 2 (*i*) (*a*) $NaK_{2.8}$, (*b*) $ICH{=}CHPh$; (*ii*) $LiBu^s$; (*iii*) ICH_2CH_2I; (*iv*) $[Mn(\eta^5-C_5H_4C{\equiv}CSnMe_3)(CO)_3]$ **7**, 5% $[PdCl_2(MeCN)_2]$; (*v*) $[Co_2(CO)_8]$

Further support for the reaction pathways in Scheme 2 comes from the observation that product **8** was not formed and

---

* The new compounds **2** and **9** both gave satisfactory IR, ^1H NMR, ^{13}C NMR and microanalytical data.

that the starting material was recovered unchanged when the coupling reaction was run in absence of palladium. The use of [Pd(PPh$_3$)$_4$] as catalyst is as effective as [PdCl$_2$(MeCN)$_2$] in promoting the coupling, implying that Pd^0 is required. These preliminary results suggest that the catalytic cycle involves sequential addition–transmetallation–reductive elimination, parallelling the pathways reported for the well known palladium-catalysed carbon–carbon bond formation.[1] To the best of my knowledge, this is the first example of an oxidative addition of palladium to an iron–iodine bond. This unprecedented result opens up a hitherto unknown aspect of palladium chemistry. On the other hand, on the basis of former experience[3a,d] and literature reports,[7] the reaction of [Co$_2$(CO)$_8$] with alkynes (either metal acetylides or cyclopentadienyl acetylides) is clean, so that the only reasonable pathway to account for the formation of the iron–carbon bond in **8** is the palladium-catalysed coupling process between **6** and **7**.* The general nature of this reaction is under investigation and has thus far been verified by the preparation of metal acetylide complexes under palladium-catalysed conditions.[8]

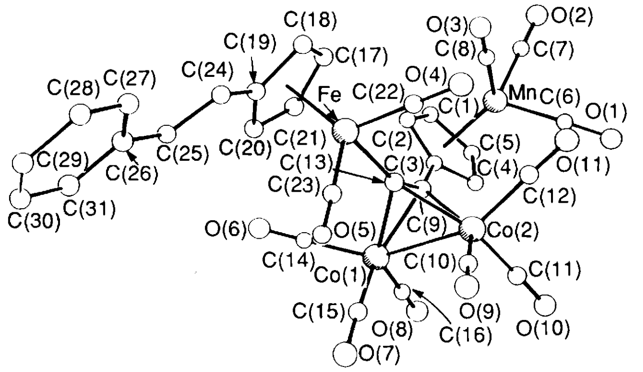


Fig. 1 Molecular structure of complex **9** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–Co(2) 2.472(1), Co(1)–C(13) 2.048(5), Co(2)–C(9) 1.968(7), Co(2)–C(13) 2.034(7), C(3)–C(9) 1.455(9), C(9)–C(13) 1.324(9), Co(1)–C(9) 1.986(6) and Fe–C(13) 1.960(7); C(9)–Co(1)–C(13) 38.3(3), C(9)–Co(2)–C(13) 38.6(3), C(3)–C(9)–C(13) 145.5(7), Co(1)–C(13)–Co(2) 74.5(2), Co(1)–C(9)–Co(2) 77.4(2) and Fe–C(13)–C(9) 149.6(6)

Acknowledgements

Dr. M. M. Miller of the Department of Chemistry at the Colorado State University is gratefully acknowledged for the X-ray structural determination of compound **9**.†

References

1 R. F. Heck, *Palladium Reagents in Organic Syntheses*, Academic Press, London, 1985; J. K. Stille, *Pure Appl. Chem.*, 1985, **57**, 1771; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508.
2 M. E. Wright and C. K. Lowe-Ma, *Organometallics*, 1990, **9**, 347 and refs. therein; J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, p. 710.
3 (*a*) C. Lo Sterzo, M. M. Miller and J. K. Stille, *Organometallics*, 1989, **8**, 2331; (*b*) C. Lo Sterzo and J. K. Stille, *Organometallics*, 1990, **9**, 687; (*c*) C. Lo Sterzo, *Organometallics*, 1990, **9**, 3185; (*d*) C. Lo Sterzo and G. Bocelli, *J. Chem. Soc., Dalton Trans.*, 1991, 1881.
4 C. Lo Sterzo, *J. Organomet. Chem.*, 1991, **408**, 253 and refs. therein.
5 G. Facchinetti and C. Floriani, *J. Chem. Soc., Chem. Commun.*, 1974, 516; F. W. C. Benfield and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1974, 1325; M. L. H. Green, *Pure Appl. Chem.*, 1978, **50**, 27; W. D. Jones and J. A. Maguire, *Organometallics*, 1985, **4**, 951; P. C. Heah, A. T. Patton and J. A. Gladysz, *J. Am. Chem. Soc.*, 1986, **108**, 1185; R. H. Crabtree, R. P. Dion, D. J. Gibboni, D. V. McGrath and E. M. Holt, *J. Am. Chem. Soc.*, 1986, **108**, 7222; G. L. Crocco and J. A. Gladysz, *J. Am. Chem. Soc.*, 1988, **110**, 6110; W. D. Jones, V. L. Kuykendall and A. D. Selmeczy, *Organometallics*, 1991, **10**, 1577.
6 SHELXTL programs used with the Nicolet R3m diffractometer and DG Eclipse S/140 computer.
7 G. A. Carriedo, V. Riera, D. Miguel, A. M. Manotti Lanfredi and A. Tiripicchio, *J. Organomet. Chem.*, 1984, **272**, C17.
8 C. Lo Sterzo and R. Crescenzi, IXth FECHEM Conference on Organometallic Chemistry, Heidelberg, 14–19th July, 1991; unpublished work.

Received 4th February 1992; Communication 2/00607C

---

* *Compound* **6**. A solution of LiBu^s (1.3 mol dm^{-3}, 5.25 cm^3, 6.82 mmol) in hexane was added dropwise by syringe to a chilled solution (−78 °C) of complex **2** (1.74 g, 6.20 mmol) in tetrahydrofuran (50 cm^3). The resulting solution was stirred at low temperature for 15 min, then ICH$_2$CH$_2$I (2.01 g, 7.45 mmol) was added as a solid and the mixture allowed to warm to room temperature with continuous stirring. It was then concentrated slightly *in vacuo*, Celite added and then evaporated to dryness. The residual solid powder was placed at the top of a column of silica gel and eluted first with hexane–ethyl acetate (4 : 1) which gave a fraction containing a small amount of unreacted **2**, and then by hexane–ethyl acetate (1 : 1) which gave a large brown fraction. Evaporation of the solvent from the latter left the product (1.74 g, 69%) as a dark solid. An analytically pure sample was recrystallized by vapour diffusion at 5 °C from chloroform and pentane. IR (CCl$_4$): ν(CO) 2039 and 1999 cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 7.47–7.28 (m, 5 H), 6.96 (d, 1 H, *J* = 16.2), 6.62 (d, 1 H, *J* = 16.2), 5.20 (t, 2 H, *J* = 2.1) and 5.05 (t, 2 H, *J* = 2.1 Hz); ^{13}C, δ 215.41, 143.98, 140.18, 133.87, 128.28, 125.18, 124.65 and 85.61 (Found: C, 44.25; H, 2.75. Calc. for $C_{15}H_{11}FeIO_2$: C, 44.35; H, 2.75%).

Compound **8**. A dimethylformamide (dmf) (30 cm^3) solution of [PdCl$_2$(MeCN)$_2$] (0.005 g, 0.02 mmol) was stirred whilst complex **2** (0.145 g, 0.358 mmol) in dmf (10 cm^3) was added with a syringe. The complex [Mn(η^5-C$_5$H$_4$C≡CSnMe$_3$)(CO)$_3$] (0.154 g, 0.394 mmol) was then added resulting in an immediate black colour. The reactants were stirred at room temperature overnight. Then diethyl ether (50 cm^3) was added and the mixture transferred to a separating funnel. The solution was washed with water (3 × 50 cm^3) and the aqueous phase back-extracted with ether (2 × 50 cm^3). The combined ether extracts were dried over magnesium sulfate and filtered. Celite was then added and the mixture evaporated to dryness *in vacuo*. The residue, added to a column of silica gel, was eluted with hexane–ether (4 : 1) to give 0.180 g (99%) of the product as a dark solid following evaporation of the solvent under vacuum. An analytically pure sample was recrystallized by slow evaporation at room temperature of a concentrated solution in chloroform. IR (CCl$_4$): ν(CO) 2044, 2018, 2000 and 1935 cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 7.47–7.28 (m, 5 H), 6.96 (d, 1 H, *J* = 16.3), 6.62 (d, 1 H, *J* = 16.3), 5.22 (t, 2 H, *J* = 2.2), 4.99 (t, 2 H, *J* = 2.2), 4.64 (t, 2 H, *J* = 2.1) and 4.52 (t, 2 H, *J* = 2.1 Hz); ^{13}C, δ 225.60, 211.95, 135.92, 133.08, 128.86, 128.63, 126.74, 118.81, 102.68, 94.67, 92.79, 83.94, 83.63, 82.37 and 81.31 (Found: C, 59.30; H, 3.05. Calc. for $C_{25}H_{15}FeMnO_5$: C, 59.30; H, 3.00%).

† *Crystal data for complex* **9**. $C_{31}H_{15}Co_2FeMnO_{11}$, $M = 792$, crystals grown by slow vapour diffusion of pentane onto a tetrahydrofuran solution of **9**, monoclinic, space group $P2_1/c$, $a = 14.5871(28)$, $b = 11.4272(20)$, $c = 18.8654(28)$ Å, $\beta = 108.56(9)°$, $U = 2981.07$ Å^3, $D_c = 1.77$ g cm^{-3}, $Z = 4$, $F(000) = 1575.7$. Data collected at −120 °C on a Nicolet R3m diffractometer with Mo-Kα radiation (λ = 0.7107 Å, μ = 21.3 cm^{-1}) using the θ–2θ scan technique. A clear, dark black crystal (0.2 × 0.2 × 0.1 mm) was mounted with vacuum grease on a glass fibre. 6094 Reflections were collected with 4549 being independent and observed [$|F_o| > 2.55\sigma(|F_o|)$]. Absorption corrections were not applied. The structure was solved by direct methods (SHELXTL[6]). All hydrogen atoms were included as idealised isotropic contributions [d(C–H) = 0.96 Å; $U_H = 1.2U$ for attached C]. The refinement converged to $R = 0.0593$ and $R' = 0.0615$, $w = [\sigma^2(F) + |g|F^2]^{-1}$ (final $g = 0.0096$).

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.