

Coupling of a 17-Electron Vinyl Complex with Chiral Recognition: Synthesis of the Pure Diastereoisomers of the Bridging Bis(carbene) Complex

$[\{\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMe}_3)\}_2\{\mu\text{-C}(\text{OMe})[\text{CH}_2]_2\text{-C}(\text{OMe})\}][\text{PF}_6]_2$

Stephane Cron, Virginie Morvan and Claude Lapinte*

Laboratoire de Chimie des Complexes de Métaux de Transition et Synthèse Organique, URA CNRS 415, Université de Rennes I, Campus de Beaulieu, 35042 Rennes, Cedex, France

The C–C bond-forming reaction by direct coupling of two chiral 17-electron metal vinyl units

$[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMe}_3)\{\text{C}(\text{OMe})=\text{CH}_2\}]^{+}$ affords the μ -bis(carbene) dimetallic complex

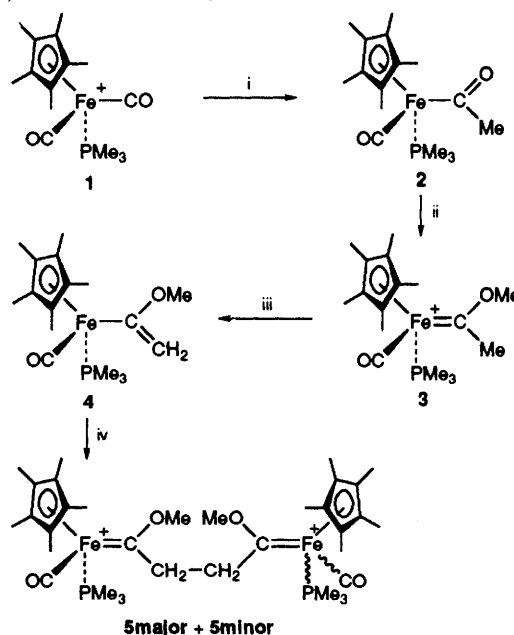
$[\{\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMe}_3)\}_2\{\mu\text{-C}(\text{OMe})[\text{CH}_2]_2\text{-C}(\text{OMe})\}][\text{PF}_6]_2$ **5** with chiral recognition (major : minor = 2 : 1); the two diastereoisomers are isolated in a pure form.

The formation of new carbon–carbon bonds is one of the most important objectives in organo-transition metal chemistry.¹ Among the different types of reaction which effect C–C bond formation, ligand–ligand coupling of unstable odd-electron organometallic species constitutes one of the least explored routes.² We report the first example of a C–C bond-forming reaction by direct coupling of two chiral 17-electron metal vinyl units $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMe}_3)\{\text{C}(\text{OMe})=\text{CH}_2\}]^{+}$ with chiral recognition. This reaction affords diastereoselectively the μ -bis(carbene) dimetallic complex $[\{\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMe}_3)\}_2\{\mu\text{-C}(\text{OMe})[\text{CH}_2]_2\text{-C}(\text{OMe})\}][\text{PF}_6]_2$ **5**, (\pm) and *meso*, which belongs to an interesting class of compounds for which few examples are known,³ especially in the case of group 18 transition metals.⁴

The metal vinyl complex $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMe}_3)\{\text{C}(\text{OMe})=\text{CH}_2\}]$ **4** was conveniently synthesized *via* a four-step procedure starting from the known compound $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2(\text{PMe}_3)][\text{PF}_6]$ **1**⁵ (Scheme 1). Addition of MeLi (1.2 equiv.) to a tetrahydrofuran (THF) suspension of the salt **1** afforded the chiral iron–acyl $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMe}_3)\{\text{C}(\text{O})\text{Me}\}]$ **2** isolated as a yellow powder in 70% yield.[†] The IR spectrum of the acyl derivative shows two characteristic absorptions due to CO bond stretching at 1578 and 1891 cm^{-1} . The iron–carbene complex $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMe}_3)\{\text{C}(\text{OMe})\text{Me}\}][\text{SO}_3\text{CF}_3]$ **3** was readily prepared by treatment of a solution of **2** (CH_2Cl_2 , -80°C , 16 h) with 1.5 equiv. of $\text{CH}_3\text{SO}_3\text{CF}_3$ and was isolated as an analytically pure orange powder (80% yield) by precipitation with diethyl ether.[†] In its ^{13}C NMR spectrum, a resonance at δ 342.2 is unequivocally assigned to the carbene carbon atom. The methoxy(methyl)carbene complex **3** was converted upon deprotonation with KOBU^{\ddagger} in the methoxyvinyl derivative $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{PMe}_3)\{\text{C}(\text{OMe})\text{CH}_2\}]$ **4**. After pentane extraction, the neutral vinyl compound was recovered as orange air-sensitive microcrystals in 85% yield.[†] The two magnetically inequivalent methylene protons of this new

organometallic species resonate as two singlets at δ 4.73 and 4.28, and the presence of the carbon atom bound to the iron centre was shown by a doublet at δ 199.9 ($^2J_{\text{CP}} = 33$ Hz) in the ^{13}C NMR spectrum.

The initial scan in the cyclic voltammogram (CV) of complex **4** from +0.5 to -0.9 V [vs. standard calomel electrode (SCE)] with a scan rate of 0.5 V s^{-1} is characterized by one irreversible process in dichloromethane with a current ratio (i_a/i_c) of 0.53. The addition of a stoichiometric amount of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2][\text{PF}_6]$ to a solution of **4** in CH_2Cl_2 (-80°C), resulted in a rapid colour change from dark brown to orange. After stirring for 6 h at -80°C , the μ -bis(carbene) bimetallic complex **5** was precipitated by addition of pentane and washed with diethyl ether. Compound **5** was isolated as a thermally stable yellow powder in 98% overall yield. The ^1H NMR spectrum of the crude solid revealed that complex **5** exists as a mixture of two diastereoisomers. The minor isomer is soluble in dichloromethane whereas the major one is insoluble in the solvent. Washing of the crude product with dichloromethane therefore allows isolation of the bis(carbene) complex **5** as two pure diastereoisomers (**5**_{major} and **5**_{minor}) in 31 and 66% yield respectively. The ^1H NMR spectrum of these two isomers shows only two distinct resonances by which they may be distinguished: the methoxymethyl resonance of the major isomer is located at δ 4.58 whereas the minor is observed upfield at δ 4.48. The methylene protons appear as a double multiplet for both compounds, but the separation of the two features is small in **5**_{major} (33 Hz) and quite large in **5**_{minor} (90 Hz). The ^{31}P NMR spectrum also exhibits two distinct



Scheme 1 Reagents and conditions: i, THF, MeLi (1.2 equiv.), -80°C ; ii, CH_2Cl_2 , $\text{CH}_3\text{SO}_3\text{CF}_3$ (1.5 equiv.), -80°C ; iii, THF, KOBU^{\ddagger} (1 equiv.), 20°C ; iv, CH_2Cl_2 , $[(\text{C}_5\text{H}_5)_2\text{Fe}][\text{PF}_6]$ (1 equiv.), -80°C

[†] Satisfactory C and H analyses were obtained for **2**, **3**, **4** and **5**. Spectroscopic data for new compounds: **2**: IR ν/cm^{-1} (CH_2Cl_2) CO 1578 and 1891; ^1H NMR (20°C , C_6D_6) δ 2.64 (s, 3H, COMe) and 1.55 (s, 15H, C_5Me_5); ^{13}C NMR (20°C , C_6D_6) δ 288.3 (d, $^2J_{\text{CP}} = 28$ Hz, COMe), 93.0 (s, C_5Me_5) and 51.7 (d, $^3J_{\text{CP}} = 7$ Hz, COMe).

3: IR ν/cm^{-1} (CD_2Cl_2) CO 1951; ^1H NMR (20°C , CH_2Cl_2) δ 4.35 (s, 3H, OMe), 2.83 (s, 3H, Me) and 1.68 (s, 15H, C_5Me_5); ^{13}C NMR (20°C , CD_2Cl_2) δ 342.2 (d, $^2J_{\text{CP}} = 27$ Hz, Fe=C), 97.7 (s, C_5Me_5), 65.8 (s, OMe), 44.9 (d, $^3J_{\text{CP}} = 2$ Hz, Me) and 9.8 (s, C_5Me_5).

4: IR ν/cm^{-1} (CH_2Cl_2) CO 1893; ^1H NMR (20°C , C_6D_6) δ 4.73 (s, 1H, =CH_a), 4.28 (s, 1H, =CH_b), 3.42 (s, 3H, OMe) and 1.62 (s, 15H, C_5Me_5); ^{13}C NMR (20°C , C_6D_6) δ 222.0 (d, $^2J_{\text{CP}} = 31$ Hz, CO), 92.2 (s, C_5Me_5), 91.6 (dd, $^1J_{\text{CH}} = 159, 146$ Hz, =CH₂) and 55.8 (q, $^1J_{\text{CH}} = 142$ Hz, OMe).

5: FAB mass spectrum $[\text{M} - \text{PF}_6]^+$, calc. 849.2, found m/z 849; IR ν/cm^{-1} (Nujol) CO 1930; ^{13}C NMR (CD_2Cl_2) δ 338.3 (d, $^2J_{\text{CP}} = 26$ Hz, Fe=C), 218.6 (d, $^2J_{\text{CP}} = 28$ Hz, CO), 100.0 (s, C_5Me_5), 67.2 (s, OMe) and 51.2 (t, $^1J_{\text{CH}} = 132$ Hz, CH₂); **5**_{major}: ^1H NMR (20°C , CD_3CN) δ 4.58 (s, 6H, OMe), 3.18 and 3.07 (dm, 4H, CH₂); ^{31}P NMR (20°C , CD_3CN) δ 30.78; **5**_{minor}: ^1H NMR (20°C , CD_3CN) δ 4.48 (s, 6H, OMe), 3.34 and 3.04 (dm, 4H, CH₂); ^{31}P NMR (20°C , CD_3CN) δ 30.88.

resonances at δ 30.78 and 30.88 for **5**_{major} and **5**_{minor} respectively. All other ^1H and ^{13}C resonances are identical for both diastereoisomers; the carbene carbon atoms resonate as a doublet 338.3 ($^2J_{\text{CP}} = 26$ Hz) and the β -carbon atoms appear as a triplet at δ 51.2 ($^1J_{\text{CH}} = 127$ Hz).

The synthesis of a μ -bis(carbene) bimetallic complex in high yield by formation of a C–C bond between two radical metal–vinyl units constitutes a new reaction for access to this class of relatively scarce compounds. Moreover, the dimerization of two 17-electron units having a CO ligand is not trivial. Indeed, the CO group is an exceptionally labile ligand in 17-electron species and most often the decoordination of the carbon monoxide induces a decomposition process.^{2,6} The stereoselectivity of the vinyl ligand coupling is also an important feature of this reaction and the stereochemistry of the bis(carbene) complex should be unambiguously assigned by X-ray analysis of one of the diastereoisomers.

On the other hand, it has been nicely shown that the chiral auxiliary $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)]^7$ exerts a powerful stereocontrol in a wide variety of reactions involving coordinated ligands, and we are actively trying to improve the stereoselectivity of this reaction by using bulkier phosphine ligands.

We are grateful to Drs P. Guénot and S. Sinbandhit (CRMPO Rennes) for mass and NMR assistance.

Received, 22nd June 1993; Com. 3/03600F

References

- 1 J. P. Collman and L. S. Hegeudus, *Principles and Application of Organotransition Metal Chemistry*, University Sciences Books, Mill Valley, CA, 1980.
- 2 For a review see: M. C. Baird, *Chem. Rev.*, 1988, **88**, 1217; N. G. Connelly and W. E. Geiger, *Adv. Organomet. Chem.*, 1984, **23**, 1.
- 3 D. W. Macomber, Mu-Huang Hung, A. G. Verma and R. D. Rogers, *Organometallics*, 1988, **7**, 2072; C. A. Toledano, A. Parlier, H. Rudler, J. C. Daran and Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, 1984, 576; W. A. Herrmann, J. Plank, J. L. Hubbard, G. W. Kriechbaum, W. Kalcher, B. Koumbouris, G. Ihl, A. Schäfer, M. L. Ziegler, H. Pfisterer, C. Pahl, J. L. Atwood and R. D. Rogers, *Z. Naturforsch., Teil B*, 1983, **38**, 1392; G. L. Miessler, S. Kim, R. A. Jacobson and R. J. Angelici, *Inorg. Chem.*, 1987, **26**, 1690.
- 4 D. H. Berry, J. E. Bercaw, A. J. Jircitano and K. B. Mertes, *J. Am. Chem. Soc.*, 1982, **104**, 4712.
- 5 S. G. Davies, S. J. Simpson and S. E. Thomas, *J. Organomet. Chem.*, 1983, **254**, C29.
- 6 *Organometallic Radical Processes*, ed. W. C. Trogler, Elsevier, Amsterdam, 1990; J. K. Kochi, *Organometallic Mechanism and Catalysis*, Academic, New York, 1978, ch. 13, pp. 341–371.
- 7 S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton and M. Whittaker, *J. Am. Chem. Soc.*, 1987, **109**, 5711; S. G. Davies, A. E. Derome and J. P. McNally, *J. Am. Chem. Soc.*, 1991, **113**, 2854; G. J. Bodwell, S. G. Davies and S. C. Preston, *J. Organomet. Chem.*, 1991, **402**, C56.