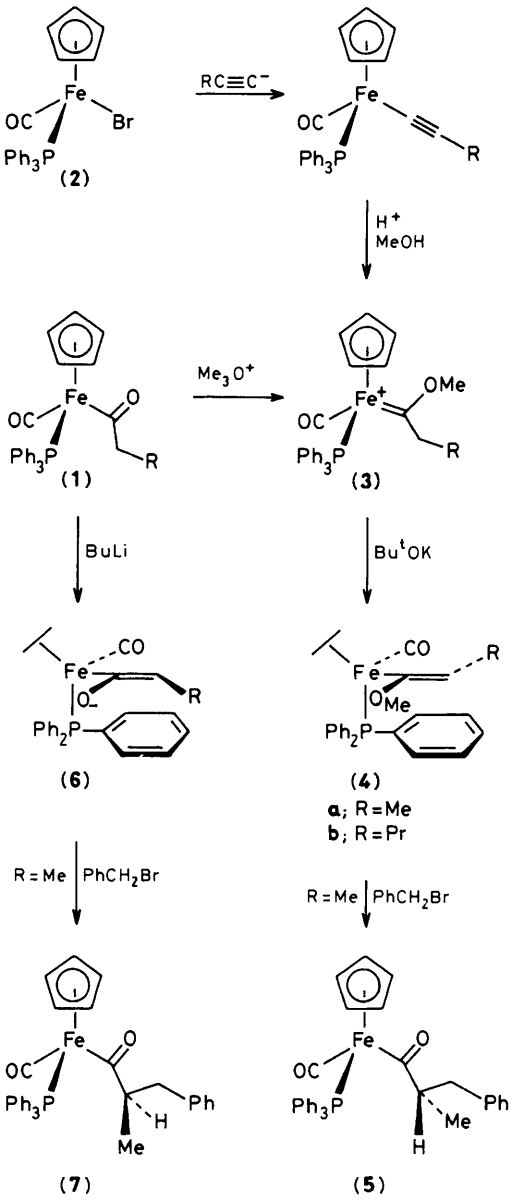
Stereoselective Carbon–Carbon Bond Formation via Alkylation of $[(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)(COMe{=}CHR)]$ (R = Me,Pr^n,Ph): *X*-Ray Crystal Structure of (*Z*)-$[(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)(COMe{=}CHMe)]$

Gordon J. Baird,[a] Stephen G. Davies,*[a] Richard H. Jones,[b] Keith Prout,[b] and Peter Warner[a]

[a] *The Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY, U.K.*
[b] *Chemical Crystallography Laboratory, 9 Parks Road, Oxford, OX1 3PD, U.K.*

$[(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)(Methoxycarbene)]^+$ complexes, prepared either from terminal acetylenes or from the corresponding acyl complexes, are stereoselectively deprotonated, as evidenced by the crystal structure of (*Z*)-$[(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)(COMe{=}CHMe)]$, to (*Z*)-methoxyvinyl complexes which can be stereoselectively alkylated under mild conditions to give elaborated acyl complexes.

$(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)(Acyl)$ complexes are potentially extremely useful in organic synthesis because of the range of mild decomplexation methods available for the conversion of such complexes into a variety of carbonyl functionalities (*e.g.* acid, ester, amide, acid halide *etc.*). We have previously described a stereoselective elaboration of such acyl complexes *via* alkylation of the enolates derived from (**1**) at low temperature.[1] We describe here the stereoselective elaboration of acyl ligands *via* methoxycarbene and methoxyvinyl complexes. This selective carbon–carbon bond formation



occurs under mild conditions (20 °C) and complements our previous method by yielding the opposite diastereoisomeric acyl complex.

Methoxycarbene complexes (**3**) are readily prepared by treatment of the bromide (**2**) with the appropriate lithium acetylide followed by protonation to the corresponding vinylidene complexes[2] and subsequent addition of methanol.[3] Alternatively they may be obtained from the corresponding acyl complexes (**1**) with trimethyloxonium tetrafluoroborate.[4] Deprotonation of these alkoxycarbene complexes[5] at −78 °C with NaOMe or KOBu^t occurs stereoselectively (>95%) to yield the (*Z*)-methoxyvinyl complexes (**4**). The stereochemistry of complexes (**4**) was assigned on the basis of nuclear Overhauser enhancements [*e.g.* for (**4a**) n.O.e. 26%] between the methoxy protons and the vinyl proton. This stereochemical assignment was confirmed for complex (**4a**) by an *X*-ray crystal structure determination shown in Figure 1.

Crystal data for (**4a**): $C_{28}H_{27}FeO_2P$, M = 482.3, triclinic, space group $P\bar{1}$, a = 9.014(2), b = 9.810(4), c = 14.057(4) Å, α = 85.59(3), β = 78.29(2), γ = 82.35(3)°, U = 1204.7 Å^3, Z = 2, D_c = 1.330 g cm^{-3}, R = 0.056 (R_w = 0.070) for 2723 observed reflections $I > 3\sigma(I)$, λ(Mo-K_α) = 0.71069 Å. Data were collected on an Enraf–Nonius CAD-4F diffractometer to θ = 25°. The crystal structure was solved by Patterson and Fourier methods. Parameters, including those for anisotropic thermal vibration were refined by large-block full-matrix refinement.[6] The majority of the hydrogen atoms were located in difference Fourier syntheses, those not found were included in their theoretical positions.† Hydrogen atoms were allowed to 'ride' on their respective carbon atoms,[6] with one overall temperature factor for the hydrogen atoms being refined.

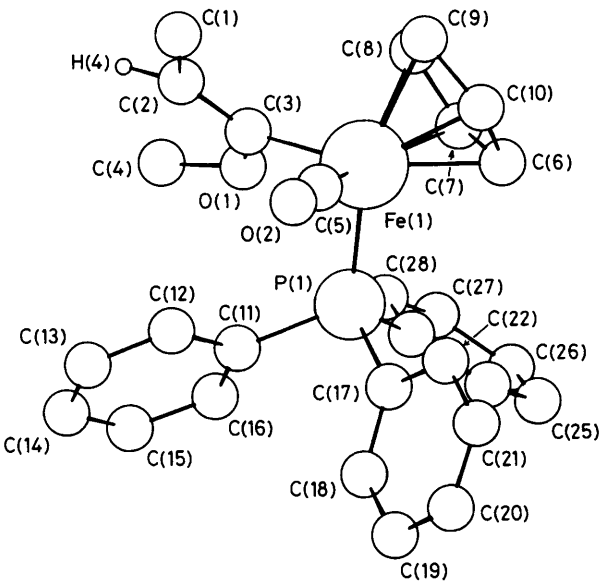


Figure 1. Molecular structure of (*Z*)-[(η^5-C_5H_5)Fe(PPh_3)(CO)-(COMe=CHMe)], (**4a**). Selected bond lengths (Å) and angles (°): Fe(1)–P(1) 2.205(1), Fe(1)–C(3) 1.974(5), Fe(1)–C(5) 1.729(5); P(1)–Fe(1)–C(3) 92.0(2), P(1)–Fe(1)–C(5) 91.7(2), C(3)–Fe(1)–C(5) 93.7(2).

The crystal structure establishes the geometry of the methoxyvinyl ligand as *Z*, that the iron centre is close to octahedral, and that the methoxy group is *anti* to the carbon monoxide ligand. Furthermore this complex provides a model for the enolates (**6**) derived from iron acyl complexes such as (**1**) and supports the postulate that one face of the enolate is shielded by a phenyl group of the triphenylphosphine ligand.[1] Complexes (**4**) are alkylated stereospecifically (>95%) by alkyl halides (*e.g.* MeI, EtI, $PhCH_2Br$) at 20 °C. For example, (**4a**) reacts with benzylbromide to give the acyl complex (**5**); the initially formed intermediate alkoxycarbene cation being demethylated by the bromide liberated. The stereochemistry of (**5**) is consistent with benzylation having occured from the unshielded face of the methoxyvinyl ligand in the *anti* oxygen to carbon monoxide conformation. It is to be noted that, because of the opposite geometries of the enolates and methoxyvinyl ligands, opposite diastereoisomers, (**7**) and (**5**) respectively, are provided *via* the two methods which therefore complement each other.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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References

1 G. J. Baird, J. A. Bandy, S. G. Davies, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1983, 1202.
2 S. Abbott, S. G. Davies, and P. Warner, *J. Organomet. Chem.*, 1983, **246**, C65.
3 B. E. Boland-Lussier and R. P. Hughes, *Organometallics*, 1982, **1**, 635.
4 M. L. H. Green, L. C. Mitchard, and M. G. Swanwick, *J. Chem. Soc. A*, 1971, 794.
5 G. Grotsch and W. Malish, *J. Organomet. Chem.*, 1983, **246**, C42.
6 D. J. Watkin and J. R. Carruthers, CRYSTALS User Guide, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1981.