Syntheses of neutral iron, ruthenium and manganese half-sandwich vinylidene complexes. Crystal structure of Fe(SnPh$_3$)(CO)(=C=CHPh)(η-C$_5$H$_5$)

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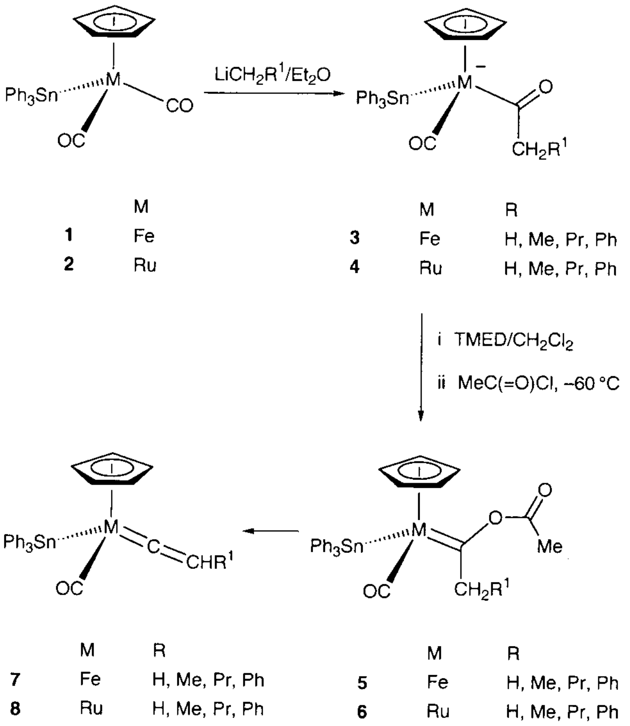
Treatment of various anionic acyls [M(SnPh$_3$)(CO)(COCH$_2$R)(η-C$_5$H$_5$)]$^-$ (M = Fe, Ru) and acyls [Mn(CO)$_2$(COCH$_2$R)(η-C$_5$H$_4$Me)]$^-$ with MeCOCl affords acyl(oxy) carbenes M(SnPh$_3$)(CO){=C(OCOMe)CH$_2$R}(η-C$_5$H$_5$) and [Mn(CO)$_2${=C(OCOMe)CH$_2$R)η-C$_5$H$_4$Me)] which formally eliminate MeCO$_2$H to form neutral half-sandwich vinylidene complexes M(SnPh$_3$)(CO)(=C=CHR)(η-C$_5$H$_5$) and complexes Mn(CO)$_2$(=C=CHR)(η-C$_5$H$_4$Me).

Vinylidene complexes L$_n$M(=C=CR^{1}R^2) have attracted a great deal of interest[1] over the last 15 years, partly due to the proposed intermediacy of vinylidene species in the Fischer–Tropsch process,[2] and also due to their ability to act as catalysts for alkyne polymerisation[3] and condensation[4] reactions. These complexes are prepared generally through either the rearrangement of alk-1-ynes at a metal centre, or through alkylation or protonation of the β-carbon of acetylide ligands. In the case of the Group 8 transition metals, the vast majority of these complexes are *cationic*. A very small number of neutral Group 7 and 8 half-sandwich vinylidene complexes are known.[5–7] We outline here a new method for the preparation of a class of *neutral* iron, ruthenium and manganese vinylidene complexes, the neutrality of which is expected to have important consequences for subsequent chemistry.

Recently, we reported the isolation of a number of unusually stable acyl(oxy) carbene species M(SnPh$_3$)(CO){=C(OCOR)Ph}(η-C$_5$H$_5$) (M = Fe, Ru; R = Me, Ph, Bu^t).[8] These are formed through the reaction of acid chlorides RCOCl with the anionic acyls [M(SnPh$_3$)(CO)(COPh)(η-C$_5$H$_5$)]$^-$. We now find that the corresponding anions [M(SnPh$_3$)(CO)(COCH$_2$R)(η-C$_5$H$_5$)]$^-$ **3**, **4** (Scheme 1) are available from the reactions of LiCH$_2$R with M(SnPh$_3$)(CO)$_2$(η-C$_5$H$_5$) **1**, **2**. These also react with MeCOCl, but while the expected acyl(oxy) carbenes M(SnPh$_3$)(CO){=C(OCOMe)CH$_2$R}(η-C$_5$H$_5$) **5** and **6** do indeed form, and are detectable by IR spectroscopy at low temperatures, the products isolated at ambient temperature are, unexpectedly, the *neutral* vinylidenes M(SnPh$_3$)(CO)(=C=CHR)(η-C$_5$H$_5$) (R = H, Pr, Me, Ph) **7** and **8**.† These products correspond to the formal loss of MeCO$_2$H from the intermediate acyl(oxy) carbenes M(SnPh$_3$)(CO){=C(OCOMe)CH$_2$R}(η-C$_5$H$_5$). The presence of protons on the carbon α to the carbene is *essential* for vinylidene formation, as is the presence of the labile acyl(oxy) substituent. We note here a previous report in which the *cationic* iron vinylidene complexes [Fe(PPh$_3$)(CO)(=C=CR$_2$)(η-C$_5$H$_5$)]$^+$ (R = H, Me) are prepared through loss of CF$_3$SO$_3$H from intermediate triflate-substituted carbenes of the form [Fe(PPh$_3$)(CO){=C(OSO$_2$CF$_3$)CHR$_2$}(η-C$_5$H$_5$)]$^+$.[9]

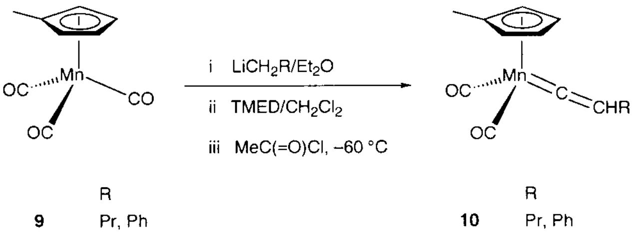
The method for vinylidene preparation presented here is versatile in that it allows the direct preparation of rare examples of unsubstituted vinylidene complexes, as well as examples bearing methyl and phenyl substituents, in a single step from readily available starting materials. Yields are good. The method also works for different metals. For instance, the corresponding reactions of the manganese compound Mn(CO)$_3$(η-C$_5$H$_4$Me) **9** (Scheme 2) afford the neutral vinylidenes M(CO)$_2$(=C=CHR)(η-C$_5$H$_4$Me) (R = Pr, Ph) **10** as red oils.‡



Scheme 1

The new complexes exhibit spectroscopic data typical for vinylidene complexes. For example, the parent complex **7** (R = H)§ shows a medium strength absorption [ν_{CO}(CH$_2$Cl$_2$) 1637 cm^{-1}] in its IR spectrum. This is attributed to the C=C stretch and signals at δ_C(CDCl$_3$) 346.2 and 105.3 in its ^{13}C NMR spectrum due to the vinylidene α- and β-carbons respectively. The presence of a singlet for the vinylidene protons in the ^{1}H NMR of the complex indicates that vinylidene rotation is facile at ambient temperature.

The nature of one compound **7** (R = Ph)¶ is further illustrated by a crystallographic study (Fig. 1), carried out in order to understand the vinylidene parameters. The Fe=C bond length of 1.744(4) Å is very short, reflecting the excellent π-acceptor properties[10] of the vinylidene fragment. The C=C bond length of 1.312(5) Å is in accord for a vinylidene complex, and reflects a bond order of *ca.* two. The vinylidene fragment itself is linear [Fe–C(7)–C(8) 179.7(3)°], and shows an orientation that corresponds both with theoretical studies[10] and with previously



Scheme 2

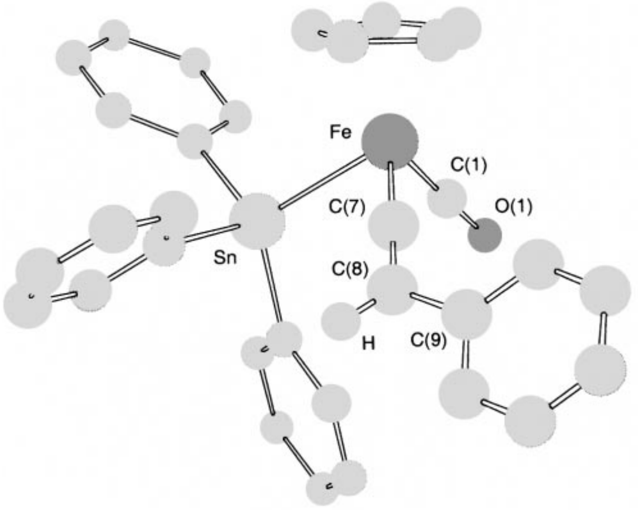


Fig. 1 Molecular structure of $Fe(SnPh_3)(CO)(=C=CHPh)(\eta\text{-}C_5H_5)$ **7** (R = Ph). Selected bond lengths (Å): Fe–C(7) 1.744(4), C(7)–C(8) 1.312(5), C(8)–C(9) 1.471(6).

reported structures of cationic iron and ruthenium vinylidene complexes.[11,12] As expected on steric grounds, the phenyl substituent occupies a position *anti* to the triphenyltin group. The vinylidene fragment does not adopt a truly horizontal conformation: the angle between the vinylidene plane and the plane defined by the centroid of the cyclopentadienyl ring, iron atom and C(7) is 73° rather than 90°. The twist is anticlockwise as viewed along C(8)–C(7)–Fe, and presumably minimizes steric interactions between the vinylidene hydrogen substituent and the triphenyltin group.

Notes and references

† $Ru(SnPh_3)(CO)(=C=CH_2)(\eta\text{-}C_5H_5)$ **8** (R = H): yellow, mp 112–113 °C. Found: C, 54.66; H, 3.81%; $[M]^+$ 570; $C_{32}H_{26}FeOSn$ requires C, 54.75; H, 3.89%; $[M]^+$ 570. IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1972s, $\nu_{C=C}$ 1637m; δ(toluene-d_8) 7.75–7.63 (m, 6H, *o*-SnPh), 7.30–7.10 (m, 9H, *m*-, *p*-SnPh), 4.78 (s, 5H, $\eta\text{-}C_5H_5$), 3.85 (s, 2H, J_{SnH} 35, $Ru=C=CH_2$); $\delta_C(CDCl_3)$ 336.3 (Ru=C), 200.3 (CO), 143.5 (*ipso*-SnPh), 136.7 (J_{SnC} 40, *o*-SnPh), 128.0 (J_{SnC} 47, *m*-, *p*-SnPh), 97.7 ($Ru=C=CH_2$), 88.4 ($\eta\text{-}C_5H_5$).

‡ $Mn(CO)_2(=C=CHPh)(\eta\text{-}C_5H_4Me)$ **10** (R = Ph): red oil. Found C, 65.26; H, 4.29%; $[M - 2CO]^+$ 236; $C_{32}H_{26}FeOSn$ requires C, 65.74; H, 4.42%; $[M - 2CO]^+$ 236. IR (light petroleum, cm^{-1}) ν_{CO} 2006s, 1952, $\nu_{C=C}$ 1647m, 1630m, 1621m, 1598m, 1575m; $\delta_H(CDCl_3)$ 7.35–7.25 (m, 2H, *o*-Ph), 7.20–7.05 (m, 3H, *m*-, *p*-Ph), 6.70 (s, 1H, =C=CH), 5.00 (m, 2H, $\eta\text{-}C_5H_4Me$), 4.95 (m, 2H, $\eta\text{-}C_5H_4Me$), 2.05 (s, 3H, Me), $\delta_C(CDCl_3)$ 380 (Mn=C), 226.5 (CO), 133.3 (*ipso*-Ph), 128.6 (*o*-, *m*-Ph), 125.2 (*p*-Ph), 124.2 (*o*-, *m*-Ph), 122.4 (=C=CHPh), 88.1 ($\eta\text{-}C_5H_4Me$); 86.4, ($\eta\text{-}C_5H_4Me$), 13.7 (Me).

§ $Fe(SnPh_3)(CO)(=C=CH_2)(\eta\text{-}C_5H_5)$ **7** (R = H): yellow, mp 101–103 °C (decomp.). Found: C, 69.67; H, 4.01%; $[M]^+$ 526; $C_{26}H_{22}FeOSn$ requires C, 59.48; H, 4.22%, $[M]^+$; 526. IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1962s, $\nu_{C=C}$ 1633m; $\delta_H(CDCl_3)$ 7.65–7.54 (m, 6H, *o*-SnPh), 7.42–7.26 (m, 9H, *m*-, *p*-SnPh), 4.89 (s, 5H, $\eta\text{-}C_5H_5$), 4.57 (s, 2H, J_{SnH} 34, $Fe=C=CH_2$); $\delta_C(CDCl_3)$ 346.2 (Fe=C), 214.4 (CO), 143.7 (*ipso*-SnPh), 136.7 (J_{SnC} 37, *o*-SnPh), 128.2 (*m*-, *p*-SnPh), 105.3 ($Fe=C=CH_2$), 85.4 ($\eta\text{-}C_5H_5$).

¶ $Fe(SnPh_3)(CO)(=C=CHPh)(\eta\text{-}C_5H_5)$ **7** (R = Ph): red–orange, mp 134–136 °C (decomp.). Found: C, 63.53; H, 4.17%; $[M]^+$ 602; $C_{32}H_{26}FeOSn$ requires C, 63.94; H, 4.36%; $[M]^+$ 602. IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1966s, $\nu_{C=C}$ 1650m, 1640m, 1626m, 1593m, 1574w; $\delta_H(CDCl_3)$ 7.63–7.53 (m, 6H, *o*-SnPh), 7.40–7.06 (m, 14H, *m*-, *p*-SnPh with Fe=C=CH*Ph*), 6.03 (s, 1H, J_{SnH} 19, Fe=C=C*H*Ph), 4.99 (s, 5H, $\eta\text{-}C_5H_5$); $\delta_C(CDCl_3)$ 354.5 (Fe=C), 213.7 (CO), 143.4 (J_{SnC} 379, *ipso*-SnPh), 136.6 (J_{SnC} 38, *o*-SnPh), 132.1 (*ipso*-Fe=C=CH*Ph*), 128.7 (*o*- or *m*-Fe=C=CH*Ph*), 128.2 (*m*-, *p*-SnPh), 126.8 (Fe=C=*C*HPh), 125.9 (*p*-Fe=C=CH*Ph*), 124.9 (*o*- or *m*-Fe=C=CH*Ph*), 85.6 ($\eta\text{-}C_5H_5$).

Crystal data for **7** (R = Ph): monoclinic, $a = 14.334(5)$, $b = 10.318(4)$, $c = 19.761(10)$ Å, $\beta = 111.09(4)°$, $U = 2727(2)$ Å^3, $Z = 4$, $D_c = 1.464$ g cm^{-3}, space group $P2_1/n$ (a non standard setting of $P2_1/c$, no. 14), Mo-Kα radiation ($\bar{\lambda} = 0.71073$ Å), μ(Mo-Kα) = 1.469 mm^{-1}, $F(000) = 1208$. Data were collected in the range $3.5 < 2\theta < 50°$ (ω-scan), 4801 independent reflections ($R_{int} = 0.0340$), final $R = 0.0355$, with allowance for the thermal anisotropy of all non-hydrogen atoms. CCDC 182/1225.

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