Syntheses of Acyloxy Carbene Complexes $M(SnPh_3)(CO)_n\{=C(OCOR)Ph\}(\eta\text{-}C_5H_5)$ (M = Mo,W, n = 2, R = Me; M = Fe, Ru, n = 1, R = Me, Ph, Bu^t) and X-Ray Crystal Structures of $Fe(SnPh_3)(CO)\{=C(OCOR)Ph\}(\eta\text{-}C_5H_5)$ (R = Me, Ph)

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Treatment of $[M(SnPh_3)(COPh)(CO)_n(\eta\text{-}C_5H_5)]^-$ (M = Fe, Ru, n = 1; M = Mo, W, n = 2) with acid chlorides R^1COCl affords carbenes $[M(SnPh_3)(CO)_n\{C(OCOR^1)Ph\}(\eta\text{-}C_5H_5)]$, which in the case of the iron and ruthenium derivatives are isolable as unusually stable crystalline solids and which react with sources of thiolate to form the new thiocarbene complexes $M(SnPh_3)(CO)_n\{C(SR^2)Ph\}(\eta\text{-}C_5H_5)$.

The importance of acyloxy carbene complexes[1] $M\{=C(OCOR^1)R^2\}L_n$ arises from their application as synthetic intermediates due to the labile nature of the carboxylate function. This allows for the ready preparation of other, often elaborate, heteroatom-substituted carbene complexes[2,3] and they are also used in organic synthesis.[4,5] Acyloxy carbene complexes are generally thermally unstable, and are usually prepared and used *in situ* at low temperatures. The reactions of oxalyl halides $C_2O_2X_2$ (X = Cl, Br) with transition metal acyl anions $[M\{C(=O)R\}L_n]^-$ is an extremely effective method for the synthesis of carbyne complexes[6–9] and it appears that these reactions proceed *via* intermediate acyloxy carbene complexes $M\{C(OCOCOX)R\}L_n$ which lose $CO_2/CO/X^-$ to form the carbyne fragment $[M\{\equiv CR\}L_n]^+$. There appears to be very little available structural information on any of these species $M\{=C(OCOR^1)R^2\}L_n$.

We demonstrate here the synthesis of isolable and structurally characterized iron and ruthenium complexes $M(SnPh_3)(CO)\{C(OCOR)Ph\}(\eta\text{-}C_5H_5)$ and demonstrate their synthetic potential. Further, while the corresponding molybdenum and tungsten complexes $M(SnPh_3)(CO)_2\{C(OCOR)Ph\}(\eta\text{-}C_5H_5)$ are not isolable, they are also good synthetic precursors.

We reported earlier that addition of LiPh to the dicarbonyls $M(SnPh_3)(CO)_2(\eta\text{-}C_5H_5)$ (**1**, M = Fe; **2**, M = Ru) results in the anionic acyl species $[M(SnPh_3)(COPh)(CO)(\eta\text{-}C_5H_5)]^-$ (**3**, M = Fe; **4**, M = Ru) and that these react with alkylating agents to give the carbene complexes $M(SnPh_3)(CO)\{=C(OEt)Ph\}(\eta\text{-}C_5H_5)$ (**5**, M = Fe; **6**, M = Ru) in good yields, Scheme 1.[10] Both complexes **5** and **6** react with I_2 to provide the carbenes **7** and **8**, the former of which is crystallographically characterised.

Acyl compounds **3** and **4** react with the acid chlorides R(CO)Cl (R = Me, Bu^t, Ph) in the presence of TMED (TMED = tetramethylethylenediamine) to give high yields of the isolable carbenes $M(SnPh_3)(CO)\{=C(OCOR)Ph\}(\eta\text{-}C_5H_5)$ (**9**–**14**), Scheme 1. Structural information on this class of carbene complex is apparently absent and so two of these compounds (**9** and **10**) were characterized crystallographically (Figs. 1 and 2).† Curiously, the orientations of the carbene are very different in **9** and **10** with torsion angles C(1)–Fe–C(25)–O(2) = +15.21° in **9** and +173.99° in **10**. The key features of these two structures **9** and **10** are that the $C_{carbene}$–OC(O)R bonds appear long [1.418(5) and 1.426(10) Å, respectively] and that in each case the OC(O)R group is orientated such that the directly bonded oxygen is not in conjugation with the carbene. This contrasts with the structure of **7** in which the $C_{carbene}$–OEt bond is short [1.344(14) Å] and in which the OEt function is orientated such that the oxygen is in conjugation with the carbene. The lack of conjugation in **9** and **10** between the carbene and oxygen allows the Fe=C bond to shorten. The M=C bond lengths in **9** and **10** [1.798(5) and 1.798(9) Å, respectively] thus appear somewhat shorter than the corresponding bond in **7** which is 1.849(10) Å. The carbene–heteroatom bond distances in the acyloxy carbene complexes as

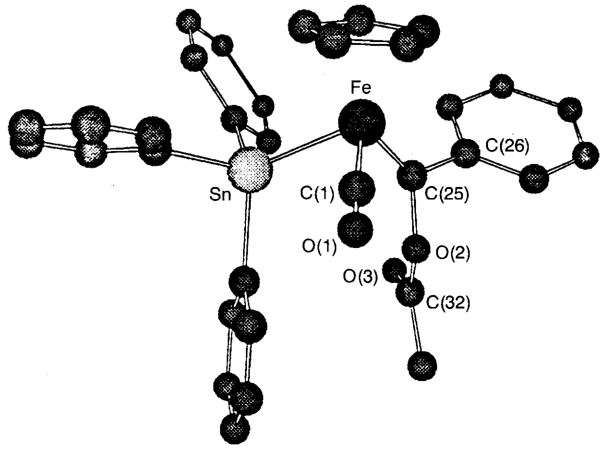
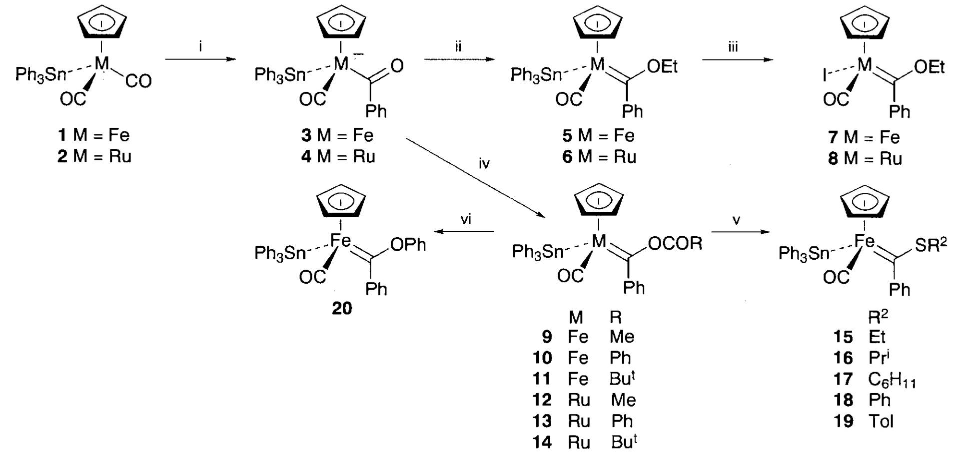


Fig. 1 Molecular structure of $Fe(SnPh_3)(CO)\{=C(OCOMe)Ph\}(\eta\text{-}C_5H_5)$ **9**. Selected bond lengths (Å), Fe–C(25) 1.798(5), C(25)–C(26) 1.489(6), C(25)–O(2) 1.418(5), C(32)–O(2) 1.374(6).



Scheme 1 *Reagents*: i, LiPh, Et_2O; ii, $[Et_3O]BF_4$, H_2O; iii, I_2, CH_2Cl_2; iv, RCOCl; v, $LiSR^2$; vi, NaOPh

presented here are in accord with the nature of the acetate function as a good leaving group from this class of complex. In effect, the acetate function could be described as being in an arrested leaving state.

The instability of most published acyloxy carbene complexes contrasts with that of all six of the compounds **9–14** which are air stable as solids and easy to handle. Complexes **9–14** are also reactive. For instance, the complex Fe(SnPh$_3$)(CO){=C(OCOBu^t)Ph}(η-C$_5$H$_5$) reacts with a number of species LiSR^2 (R^2 = Et, Pr^i, C$_6$H$_{11}$, Ph, Tol) with displacement of Bu^{t}CO$_2{}^-$ to form new thiocarbene complexes Fe(SnPh$_3$)(CO){=C(SR^2)Ph}(η-C$_5$H$_5$) in excellent yields, Scheme 1. A further example is given by the reaction of Fe(SnPh$_3$)(CO){C(OCOBu^t)Ph}(η-C$_5$H$_5$) with NaOPh. The resulting product Fe(SnPh$_3$)(CO){=C(OPh)Ph}(η-C$_5$H$_5$) **20** is one of a small number of phenoxy carbene complexes.

Reaction of the related molybdenum and tungsten acyl anions [M(SnPh$_3$)(CO)$_2${=C(O)Ph}(η-C$_5$H$_5$)]$^-$ **21–22** with MeCOCl affords the neutral acyloxy carbenes M(SnPh$_3$)(CO)$_2${=C(OCOMe)Ph}(η-C$_5$H$_5$) **23–24** (Scheme 2) but in these cases, they are not isolable. Facile decomposition to the carbyne complexes M(CO)$_2$(≡CPh)(η-C$_5$H$_5$) occurs at temperatures above −40 °C.[11] However, they are still useful from a synthetic point of view and they react at low temperature with NaSAr (Ar = Ph, Tol) to form the new thiocarbene complexes M(SnPh$_3$)(CO)$_2${=C(SAr)Ph}(η-C$_5$H$_5$) **25–28**. These compounds are not formed by more conventional thiolysis reactions such as those of M(SnPh$_3$)(CO)$_2${C(OEt)Ph}(η-C$_5$H$_5$) with thiolate reagents.

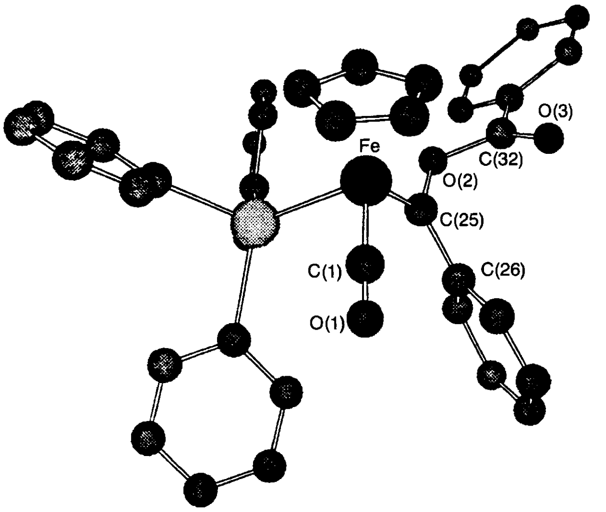
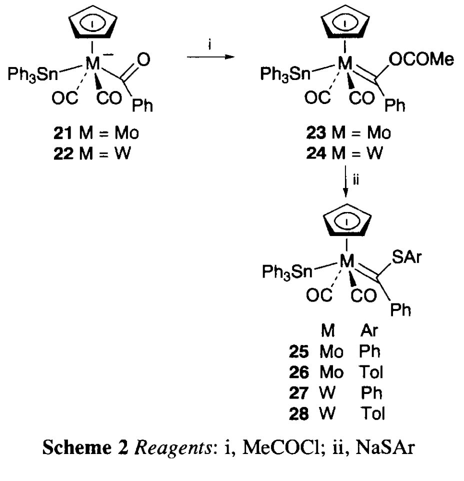


Fig. 2 Molecular structure of Fe(SnPh$_3$)(CO){=C(OCOPh)Ph}(η-C$_5$H$_5$) **10**. Selected bond lengths (Å), Fe–C(25) 1.798(9), C(25)–C(26) 1.485(12), C(25)–O(2) 1.426(10), C(32)–O(2) 1.358(10).



Scheme 2 *Reagents*: i, MeCOCl; ii, NaSAr

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Footnotes

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† *Selected data* for Fe(SnPh$_3$)(CO){C(OCOMe)Ph}(η-C$_5$H$_5$) **9**: (Found C, 61.50; H, 4.30%, [M − CO]$^+$, 620. C$_{33}$H$_{28}$FeO$_3$Sn requires C, 61.25; H, 4.36%, [M − CO]$^+$, 620). IR ν_{CO}/cm^{-1} (CH$_2$Cl$_2$) 1938s, 1747m; ^{1}H NMR (CDCl$_3$, −50 °C, isomer ratio major : minor 3 : 1) major isomer δ 7.42–7.28 (6 H, m, *o*-SnPh), 7.27–7.05 (12 H, m, *m,p*-SnPh with *m,p*-=C*Ph*), 6.96–6.88 (2 H, m, *o*-=C*Ph*), 4.95 (5 H, s, η-C$_5$H$_5$), 2.20 (3 H, s, Me); minor isomer δ 7.63–7.57 (6 H, m, *o*-SnPh), 7.27–7.05 (12 H, m, *m,p*-SnPh with *m,p*-=C*Ph*), 6.96–6.88 (2 H, m, *o*-=C*Ph*), 4.79 (5 H, s, η-C$_5$H$_5$), 1.48 (3 H, s, Me); ^{13}C NMR (CDCl$_3$, −50 °C) major isomer δ 306.4 (Fe=C), 217.7 (CO), 165.6 (*C*O$_2$Me), 153.7 (*i*-=C*Ph*), 142.6 (*i*-Sn*Ph*), 136.3 (*o*-Sn*Ph*), 130.3–127.8 (*m,p*-Sn*Ph* with *m,p*-=C*Ph*), 124.9–122.9 (*o*-=C*Ph*), 86.8 (η-C$_5$H$_5$), 21.8 (Me); minor isomer δ 305.3 (Fe=C), 216.3 (CO), 165.1 (*C*O$_2$Me), 147.0 (*i*-=C*Ph*), 143.9 (*i*-Sn*Ph*), 136.8 (*o*-Sn*Ph*), 130.3–127.8 (*m,p*-Sn*Ph* with *m,p*-=C*Ph*), 124.9–122.9 (*o*-=C*Ph*), 87.4 (η-C$_5$H$_5$), 20.8 (Me).

Crystal data for **9**: monoclinic, a = 12.340(3), b = 16.714(5), c = 13.744(5) Å, β = 92.44(3)°, U = 2832(2) Å^3, Z = 4, D_c = 1.518 g cm^{-3}, space group $P2_1/n$ (a non standard setting of $P2_1/c$ C^5_{2h}, No. 14), Mo-Kα radiation ($\bar{\lambda}$ = 0.71073 Å), μ(Mo-Kα) = 1.426 mm^{-1}, F(000) = 1304. Data were collected in the range $3.5 < 2\theta < 45°$ (ω-scan), 2943 independent reflections [$|F|/\sigma(|F|) > 4.0$], final R 0.0342, with allowance for the thermal anisotropy of all non-hydrogen atoms.

Selected data for Fe(SnPh$_3$)(CO){C(OCOPh)Ph}(η-C$_5$H$_5$) **10**: (Found C, 64.59; H, 4.18%, [M]$^+$ 710. C$_{38}$H$_{30}$FeSnO$_3$ requires C, 64.36; H, 4.26%, [M]$^+$ 710). IR ν_{CO}/cm^{-1} (CH$_2$Cl$_2$) 1938s, 1721m; ^{1}H NMR (CDCl$_3$, −50 °C, isomer ratio 7 : 1) major isomer δ 7.64–7.52 (6 H, m, *o*-Sn*Ph*), 7.44–7.15 (17 H, m, *m,p*-SnPh with *m,p*-=C*Ph* and CO$_2$*Ph*), 7.13–6.99 (2 H, m, *o*-=C*Ph*), 5.03 (5 H, s, η-C$_5$H$_5$); minor isomer δ 7.51–7.45 (6 H, m, *o*-SnPh), 7.44–7.15 (17 H, m, *m,p*-SnPh with *m,p*-=C*Ph* and CO$_2$*Ph*), 7.13–6.99 (2 H, m, *o*-=C*Ph*), 4.87 (5 H, s, η-C$_5$H$_5$); ^{13}C NMR (CDCl$_3$, −50 °C) major isomer only, δ 305.7 (Fe=C), 217.9 (CO), 160.8 (*C*O$_2$Ph), 154.3 (*i*-=CPh), 143.3 (*i*-SnPh), 136.4 (*o*-SnPh), 133.6–127.8 (*m,p*-SnPh and *m,p*-=C*Ph* with CO$_2$*Ph*), 124.8–123.4 (*o*-=C*Ph*), 87.0 (η-C$_5$H$_5$).

Crystal data for **10**: monoclinic, a = 12.090(2), b = 18.572(5), c = 15.290(4) Å, β = 112.030(10)°, U = 3182.5(13) Å^3, Z = 4, D_c = 1.480 g cm^{-3}, space group $P2_1/c$ (C^5_{2h}, No. 14), Mo-Kα radiation ($\bar{\lambda}$ = 0.71073 Å), μ(Mo-Kα) = 1.276 mm^{-1}, F(000) = 1432. Data were collected in the range $3.5 < 2\theta < 45°$ (ω-scan), 3300 independent reflections [$|F|/\sigma(|F|) > 4.0$], final R 0.0596, with allowance for the thermal anisotropy of all non-hydrogen atoms.

Atomic coordinates, bond lengths and angles, and thermal parameters for both **9** and **10** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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