Photochemical Reactions of [*cis*-Fe(H)$_2$(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$] with Thiophenes: Insertion into C–H and C–S Bonds

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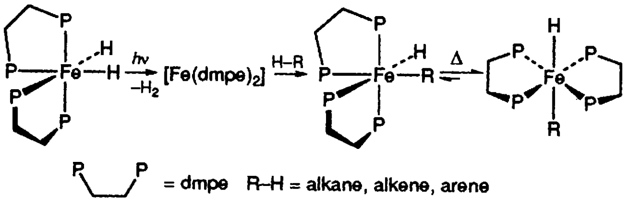
Photolysis of [*cis*-Fe(H)$_2$(dmpe)$_2$] [dmpe = 1,2-bis(dimethylphosphino)ethane] in the presence of simple thiophenes gives products formed by insertion of the iron centre into both C–H and C–S bonds; the crystal structure of [Fe(SCMeCHCHCH)(dmpe)$_2$] is a planar 'ferrathiacycle' but bond lengths and ^{1}H NMR spectroscopy indicate that this ring is best described as a localised diene structure rather than a 'ferrathiabenzene' with delocalised π-system.

The removal of sulfur from fossil fuels is of great commercial and environmental importance[1] and, of the S-containing compounds present, thiophenes are the most difficult to desulfurise.[2] To help elucidate mechanistic aspects of the hydrodesulfurisation (HDS) of thiophenes recent attention has focused on organometallic compounds as models for potential intermediates.[3] Complexes such as [Mn(C$_4$H$_4$S)(CO)$_3$]$^+$,[4] [Ir(C$_5$Me$_5$)(C$_4$H$_4$S)][5] and [Re(C$_5$Me$_5$)(SC$_4$H$_4$)(CO)$_2$],[6] containing η^5-, η^4- and S-bound thiophene respectively, as well as [(C$_5$Me$_5$)Ir(SCMeCHCHCMe)][5] and [(C$_5$Me$_5$)(Me$_3$P)Rh(SCHCHCHCH)][7] have been reported. The latter complexes are particularly interesting since C–S bond cleavage is presumably a key step in the HDS process. The chemistry of σ-thienyl complexes, formed by insertion into a C–H bond of thiophene, has been described[8] as 'poorly developed'. Reports of thienyl products have appeared[9,10] since and recently Dong *et. al.* described the formation of both C–H and C–S insertion products on photolysis of [Rh(C$_5$Me$_5$)(PMe$_3$)(H)$_2$] in the presence of thiophenes.[10]

We have studied the photochemically induced reactions of [*cis*-Fe(H)$_2$(dmpe)$_2$] with organic substrates such as alkanes, alkenes and arenes to afford C–H insertion products (Scheme 1).[11] The transient, coordinatively unsaturated 16-electron species 'Fe(dmpe)$_2$' proposed in Scheme 1 is highly reactive and inserts even into the C–H bond of methane[12] although, from competition experiments, the C–H bonds of alkenes are more reactive than the corresponding alkanes. Given the activity of [*cis*-Fe(H)$_2$(dmpe)$_2$] towards C–H activation and the relatively few reports of C–H insertion products of thiophenes we have examined the photochemical reaction between these reagents and now give a report of our findings.

When thiophene–hexane or 2-methylthiophene–hexane (1:2 v/v) solutions of [*cis*-Fe(H)$_2$(dmpe)$_2$] were irradiated at 248 K, ^{31}P{^{1}H} NMR spectroscopy showed a complex reaction mixture containing a number of *cis*- and *trans*-adducts. If the reaction mixture was warmed to 273 K (or the photolysis performed at 273 K) the ^{31}P{^{1}H}, ^{1}H and ^{13}C NMR spectra show resonances for two major products which can be assigned to [Fe(SCRCHCHCH)(dmpe)$_2$] and [*trans*-FeH(CCHCHCRS)(dmpe)$_2$] (for thiophene, R = H; for 2-methylthiophene, R = Me) formed by C–S and C–H insertion, respectively (Scheme 2). Crystals of the C–S insertion product, [Fe(SCMeCHCHCH)(dmpe)$_2$], were obtained and the result of a X-ray diffraction study is shown in Fig. 1.†

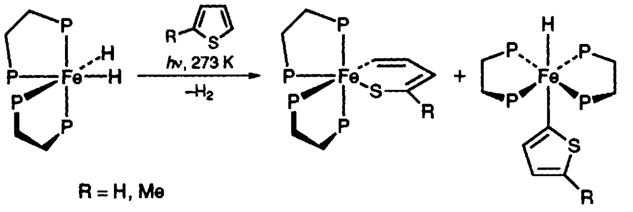
Photolysis of [*cis*-Fe(H)$_2$(dmpe)$_2$] in 3-methylthiophene gives [Fe(SCHCHCMeCH)(dmpe)$_2$] and [Fe(SCHCMeCHCH)(dmpe)$_2$] in a 1:8 ratio (by ^{31}P{^{1}H} NMR spectroscopy) formed by 1-2- and 1-5-insertion, respectively, as well as *cis*- and [*trans*-FeH(C$_5$H$_4$S)(dmpe)$_2$] and two other products containing *cis*-phosphines. The *cis*-hydrido complexes slowly isomerise to the *trans*-adducts at ambient temperature.



Scheme 1

The ^{31}P{^{1}H} NMR spectra‡ of the C–S insertion products are characterised by an unusually large $^2J_{PP}$ coupling constant of *ca.* 260 Hz between the *trans*-phosphorus atoms. The C–S insertion products also exhibit observable ^{31}P coupling to the carbon atom bound to the metal ($^3J_{PC}$ *ca.* 16–35 Hz) and to the proton bound to this carbon ($^4J_{PH}$ *ca.* 3–25 Hz). For the C–H insertion products, the *trans* coupling between phosphorus atoms is smaller ($^2J_{PP}$ 120 Hz), and ^{31}P coupling to the protons of the thienyl ring is less evident.

Chen and coworkers have prepared[5] the 'iridathiabenzene'



Scheme 2

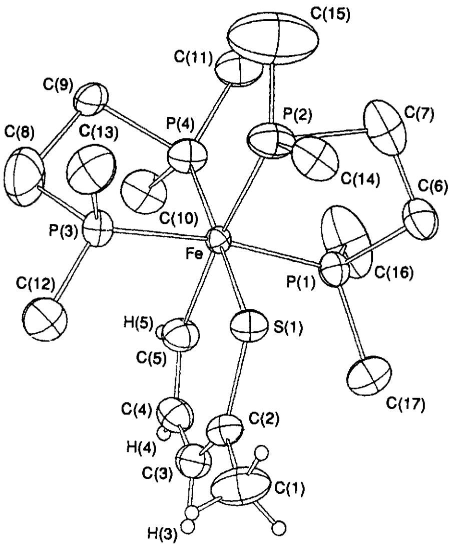


Fig. 1 The crystal structure of [Fe(SCMeCHCHCH)(dmpe)$_2$] with thermal elipsoids at the 30% probability level. The H atoms of the dmpe ligand were not refined, the methyl H atoms of the ferrathiacycle were fixed in calculated positions and H(3)–H(5) were refined. Selected bond lengths (Å): Fe–P(1) 2.201(3), Fe–P(2) 2.230(3), Fe–P(3) 2.199(3), Fe–P(4) 2.203(3), Fe–S 2.335(3), Fe–C(5) 1.996(10), S(1)–C(2) 1.742(10), C(2)–C(3) 1.351(13), C(3)–C(4) 1.439(16) and C(4)–C(5) 1.318(15); selected angles (°): P(1)–Fe–P(2) 90.9(1), P(3)–Fe–P(4) 90.8(1), P(1)–Fe–P(3), 172.2(1), S(1)–Fe–P(4) 177.2(1), C(5)–Fe–P(2) 174.4(3), C(5)–Fe–S(1) 90.9(3), Fe–S(1)–C(2) 114.0(3), S(1)–C(2)–C(3) 125.1(8), C(2)–C(3)–C(4) 127(1), C(3)–C(4)–C(5) 129(1), C(4)–C(5)–Fe 132.9(9).

complex [(C_5Me_5)Ir(SCMeCHCHCMe)]. The presence of a delocalised π-system in this iridium complex is supported by low field chemical shifts for the protons of the metallocycle ring and by diffraction studies which show a planar ring and Ir–S, Ir–C, C–C and C–S distances intermediate between reported single- and double-bond lengths. In contrast, NMR and X-ray studies on [(C_5Me_5)(Me_3P)Rh(SCMeCHCHCH)][7] and [(Me_3P)$_3$Ir(SCHCHCHCH)Cl][13] show metallocycle proton resonances shifted upfield with respect to 2-methylthiophene and a ring with a localised diene structure. The chemical shift of the ferrathiacycle protons are between those reported for the iridathiabenzene and the rhodium complex but closer to those expected for a diene structure. The crystal structure of [Fe(SCMeCHCHCH)(dmpe)$_2$] shows an almost planar ferrathiacycle; the largest torsion angle around the ring is 3.5° [C(5)–C(4)–C(3)–C(2)] and the largest deviation from the plane defined by Fe–S–C(2)–C(3)–C(4)–C(5) is 0.027 Å for the sulfur atom. In contrast, [(C_5Me_5)(Me_3P)Rh(SCMeCHCHCH)] contains a puckered rhodathiacycle in which the rhodium atom lies 0.7 Å out of the plane.[7] The C–C bond lengths in [Fe(SCMeCHCHCH)(dmpe)$_2$] show considerable alteration [C(4)–C(5) = 1.318, C(3)–C(4) = 1.439 and C(2)–C(3) = 1.351 Å] and the Fe–S distance of 2.335(3) Å is only slightly shorter than the 2.349(1) Å observed[14] in the thiolato-complex, [*cis*-Fe(SCH_2CH_2S)(dmpe)$_2$]. This structural study suggests that the complex is probably better described as a diene rather than a delocalised ferrathiabenzene.

For thiophene, C–H insertion can occur at the 2- or 3-carbon atoms while for 2-methylthiophene, insertion at the 3-, 4- or 5-positions is possible. The predominant chemical reactivity of simple thiophenes occurs at the carbon adjacent to, and activated by, the sulfur atom. The isotopically labelled substrates 2,5-dideuteriothiophene and 2-deuterio-5-methylthiophene gave the C–D insertion products [*trans*-FeD(C_4H_2DS)(dmpe)$_2$] and [*trans*-FeD(C_5H_5S)(dmpe)$_2$] respectively on photolysis with [*cis*-Fe(H)$_2$(dmpe)$_2$] at 273 K. Crystals of the C–H insertion adduct of 2-methylthiophene were also obtained and, although they do show that the thienyl ring is bound at the carbon adjacent to sulfur, they exhibit disorder which has so far prevented satisfactory refinement.

In summary, photolysis of [*cis*-Fe(H)$_2$(dmpe)$_2$] with simple thiophenes at 273 K gives C–H and C–S insertion products. Prolonged photolysis (15 h) of the thiophene product mixture at 273 K does not appear to affect the relative ratios of the C–H and C–S adducts suggesting that they are stable under the photochemical conditions of the experiment. The high selectivity shown by product ratio for the 2- and 3-methylthiophene reactions implies that C–S insertion is subject to steric control and preliminary results using the bulkier dibenzothiophene ligand indicate that only a C–H insertion product is formed at 273 K. In contrast, C–H insertion appears to be controlled by electronic factors and occurs predominantly at the carbon adjacent to the S atom and we find that the *cis*-hydrido adduct is the kinetic product of the reaction which isomerises to the thermodynamically stable *trans*-hydrido species.

We gratefully acknowledge the support of the Australian Research Council for funding these studies.

Received, 2nd November 1993; Com. 3/06550B

Footnotes

† *Crystal data* for [Fe(SCMeCHCHCH)(dmpe)$_2$]: $C_{17}H_{37}FeP_4S$, *M* = 453.28, orthorhombic, space group $P2_12_12_1$, *a* = 9.289(3), *b* = 13.886(3), *c* = 17.958(6) Å, *Z* = 4, *R* = 0.0478 (1622F). Cell constants were determined by a least squares fit to the θ values of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer with a graphite monochromator. Data were reduced and Lorentz, polarisation and decomposition corrections applied using the Enraf-Nonius Structure Determination Package.[15] The structure was solved by direct methods using SHELX-86S and was refined by full-matrix least-squares analysis using SHELX-76.[16] Configurational disorder amongst the dmpe ligands was apparent and the methyl and methylene carbon atoms of these ligands were refined with partial occupancies. Of the ferrathiacycle H atoms, H(3)–(5) were refined and the H atoms of the methyl group were fixed in calculated positions (C–H, 0.97 Å). The H atoms of the phosphines were omitted because of the disorder amongst the dmpe ligands. Atomic coordinates, bond lengths and angles, and thermal parameters have been desposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ *Selected NMR spectroscopic data* at 300K in [$^2H_8$]THF unless stated. ^{31}P NMR spectra (162.0 MHz) were referenced internally to the high field resonance of residual [*cis*-Fe(H)$_2$(dmpe)$_2$] at δ 66.9.[17] ^1H NMR (400.1 MHz) spectra were referenced to solvent resonances and values of J_{HH} were determined after decoupling ^{31}P. Coupling constants are in Hz and their signs are not implied.

[Fe(SCHCHCHCH)(dmpe)$_2$]: $^{31}P\{^1H\}$ NMR δ 68.6 (ddd, J_{PP} 9.6, 35.5, 40.9), 65.4 (ddd, J_{PP} 20.9, 40.9, 266.1), 62.9 (ddd, J_{PP} 35.5, 28.9, 266.1), 48.3 (ddd, J_{PP} 9.6, 20.9, 28.9); ^1H NMR δ 7.38 (dddd, C-H, J_{PH} 23, 3, 3, J_{HH} 11.6), 6.81 (m, C–*H*, J_{HH} 11.6, 6.7), 5.70 (dd, C–*H*, J_{HH} 6.8, 9.5), 5.33 (m, C–*H*, J_{HH} 9.5).

[Fe(SCMeCHCHCH)(dmpe)$_2$]: $^{31}P\{^1H\}$ NMR δ 68.4 (ddd, J_{PP} 9.5, 35.9, 40.7), 65.2 (ddd, J_{PP} 21.0, 41.2, 261.6), 62.7 (ddd, J_{PP} 28.5, 35.9, 261.6), 47.8 (ddd, J_{PP} 9.5, 21.0, 28.4); ^1H NMR δ 7.21 (dddd, C–*H*, J_{PH} 22, 4, 4, J_{HH} = 11.6), 6.82 (m, C–*H*, J_{HH} 11.7, 6.7), 5.71 (d, C–*H*, J_{HH} 6.8). [Fe(SCHCMeCHCH)(dmpe)$_2$]: $^{31}P\{^1H\}$ NMR δ 68.4 (ddd, J_{PP} 8.6, 34.3, 40.7), 64.1 (ddd, J_{PP} 20.9, 40.7, 268.5), 60.9 (ddd, J_{PP} 29.4, 34.3, 268.5), 48.5 (ddd, J_{PP} 8.6, 20.9, 29.4); ^1H NMR δ 7.54 (dddd, C–*H*, J_{PH} 22, 3, 3, J_{HH} 11.6), 6.73 (m, C–*H*, J_{HH} 11.7), 5.07 (s, br C–*H*). [*trans*-FeH(CCHCHCHS)(dmpe)$_2$]: $^{31}P\{^1H\}$ NMR δ 74.0 (s); ^1H NMR δ −19.83 (q, Fe–*H* J_{PH} 49.1). [*trans*-FeD(CCHCHCDS)(dmpe)$_2$] (in 2,5-dideuteriothiophene–[$^2H_8$]THF mixture): $^{31}P\{^1H\}$ NMR δ 74.1 (t, J_{PD} 7.3). [*trans*-FeH(CCHCHCMeS)(dmpe)$_2$]: $^{31}P\{^1H\}$ NMR δ 74.0 (s); ^1H NMR δ −19.86 (q, Fe–*H* J_{PH} 48.0). [*trans*-FeD(CCHCHCMeS)(dmpe)$_2$] (in 2-deuterio-5-methylthiophene–[$^2H_8$]THF mixture): $^{31}P\{^1H\}$ NMR δ 74.2 (t, J_{PD} 7.4).

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