Preparation and Mössbauer Spectra of Some Cyclopentadienyl Iron Complexes Containing a Chelating Diphosphine Ligand

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Convenient methods of preparing complexes of the type $(C_5H_5)Fe(dppe)X$ (dppe = $Ph_2PCH_2CH_2PPh_2$) are reported and some new complexes are described. The ^{57}Fe and (for X = $SnCl_3$, $SnBr_3$, and SnI_3) the ^{119}Sn Mössbauer spectra of these complexes have been recorded, and are discussed in relation to the spectra of analogous $C_5H_5Fe(CO)_2X$ and $C_5H_5Fe(CO)(L)X$ complexes (L = monodentate phosphine) which have been previously studied.

THE substitution of carbonyl groups by tertiary phosphines in complexes of the type $C_5H_5Fe(CO)_2X$ has been well studied, and many such substituted complexes have been characterised.[1-4] Disubstituted complexes are, however, more difficult to prepare by direct substitution than are monosubstituted complexes, and u.v. irradiation or extended periods of reflux in high boiling solvents are often required.[2,4,5] In consequence, direct substitution can only be used as a method of preparing disubstituted complexes of the type $C_5H_5FeL_2X$ in the fairly restricted number of cases where the products can survive the reaction conditions needed to effect substitution.

In the case of the potentially bidentate ligand, bis-diphenylphosphinoethane (dppe), the only complexes of the type $C_5H_5Fe(dppe)X$ to have been prepared (all by substitution) are those where X = Cl,[6] I,[7] $SnMe_3$,[8] C_2F_5,[9] or $(CF_3)_2CF$.[9] The choice of reaction conditions

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is particularly important if these complexes are to be obtained in good yield, since a number of other types of complex can be formed. Thus whereas reaction of $C_5H_5Fe(CO)_2Cl$ with dppe in benzene under u.v. irradiation gives $C_5H_5Fe(dppe)Cl$,[6] $[\{C_5H_5Fe(CO)_2\}_2(dppe)]Cl_2$ is obtained on refluxing in benzene in the absence of u.v. irradiation [1] and $[C_5H_5Fe(dppe)CO]Cl$ if the reactants are irradiated in tetrahydrofuran (thf) or acetone.[10]

In this paper we report an indirect method of preparing $C_5H_5Fe(dppe)Cl$ which gives this complex in good yield as a 1 : 1 chloroform adduct. We have used this complex to prepare a number of other new disubstituted complexes by indirect means. Where these new complexes have been obtained in sufficient yield their Mössbauer spectra have been recorded, since these are of interest in relation to the spectra of analogous unsubstituted and monosubstituted derivation which have been previously studied.[4,11–13]

RESULTS AND DISCUSSION

Preparation of New Complexes.—Reaction of thallium cyclopentadienide with $FeCl_2(dppe)$ in benzene at room temperature gives $C_5H_5Fe(dppe)Cl$ in up to 80% yield. Ferrocene is the main by-product of the reaction and the required complex may be readily separated from this impurity by column chromatography using chloroform as the eluant. Isolated in this way the complex is obtained as a 1 : 1 chloroform adduct, which was used for all further preparations. $FeCl_2(dppe)$ itself has not been previously reported but is readily obtained from the reaction of anhydrous ferrous chloride with dppe in acetone–chloroform (see Experimental section).

$C_5H_5Fe(dppe)SnCl_3$ was prepared by means of the well known insertion reaction [14,15] using anhydrous $SnCl_2$, and the other SnX_3 complexes by the similar reactions of an excess of anhydrous SnX_2 with either $C_5H_5Fe(dppe)Cl,CHCl_3$ or $C_5H_5Fe(dppe)SnCl_3$. $C_5H_5Fe(dppe)Me$ and $C_5H_5Fe(dppe)H$ were prepared respectively by the action of MeMgI and $NaBH_4$ on $C_5H_5Fe(dppe)Cl,CHCl_3$ in thf solution. Finally $C_5H_5Fe(dppe)SnMe_3$ was prepared by the action of MeMgI on $C_5H_5Fe(dppe)SnCl_3$. Direct substitution of dppe into $C_5H_5Fe(CO)_2SnMe_3$ under the influence of u.v. irradiation provides an alternative route to this complex.[4]

All the new complexes reported are air-stable crystalline materials, except for $C_5H_5Fe(dppe)H$ which deteriorates slowly in air.

Mössbauer Spectra.—(a) *The* ^{57}Fe *Resonance.* In a previous Mössbauer study of complexes of the type $C_5H_5Fe(CO)_2X$, changes in the ^{57}Fe centre shift were attributed to differences in π-acceptor ability of the various X ligands studied.[12] This assumption gives an ordering of the ligands which is very similar to that obtained using other spectroscopic techniques. Applying this approach to the series of complexes studied here leads to the reasonable conclusion that dppe is a poorer π-accepting ligand than the two CO groups which it replaces, since δ_{Fe} is consistently higher for the dppe substituted complexes than for the unsubstituted complexes (Table 1). However the approach is almost certainly an oversimplification, since other Mössbauer studies on related complexes have shown that σ-bonding effects are also important, and may be dominant in determining the value of δ_{Fe} in some cases.[4,13]

TABLE 1

^{57}Fe Mössbauer parameters [a]

Compound	δ	Δ
$C_5H_5Fe(CO)_2Cl$ [b]	0·49	1·88
$C_5H_5Fe(dppe)Cl,CHCl_3$ [c]	0·70	1·97
$C_5H_5Fe(CO)_2SnCl_3$ [d]	0·39	1·86
$C_5H_5Fe(dppe)SnCl_3$ [c]	0·59	1·75
$C_5H_5Fe(dppe)SnBr_3$ [c]	0·61	1·84
$C_5H_5Fe(CO)_2SnMe_3$ [e]	0·36	1·75
$C_5H_5Fe(dppe)SnMe_3$ [c]	0·59	1·63
$C_5H_5Fe(CO)_2Me$ [c]	0·11	1·75
$C_5H_5Fe(dppe)Me$ [c]	0·53	1·82
$[C_5H_5Fe(CO)_3]^+$ [f]	0·27	1·78
$[C_5H_5Fe(dppe)CO]^+$ [c]	0·60	1·09
$C_5H_5Fe(dppe)SnI_3$ [c]	0·63	1·80
$C_5H_5Fe(dppe)H$ [c]	0·50	1·86

[a] All centre shift values are quoted relative to sodium nitroprusside at 295 K, with the sample at *ca.* 80 K. Line width at half height *ca.* 0·3 mm s^{-1}. [b] Ref. 11. [c] This work. [d] Ref. 16. [e] Ref. 4. [f] Ref. 12.

Indeed, in the complexes $C_5H_5Fe(dppe)H$ and $C_5H_5Fe(dppe)CH_3$ π-bonding effects can be safely ignored, and the relatively low values of δ_{Fe} for these two complexes as compared to the other dppe substituted complexes can be attributed to the high σ-donor ability of the ligands H^- and CH_3^-.[17]

The ^{119}Sn *Resonance.*—The sign of e^2qQ for $C_5H_5Fe(CO)_2SnCl_3$ has recently been determined as being positive,[13,15] and it seems most probable [18] that it is positive also for $C_5H_5Fe(dppe)SnCl_3$ and for the other trihalogenotin complexes studied here. Hence V_{zz} is negative and, assuming that the quadrupole splitting arises largely from a p-electron imbalance in the four tin–ligand bonds, an increase in the magnitude of the observed quadrupole splittings in the disubstituted complexes would imply that the iron atom becomes a better σ-donor towards the tin $5p_z$ orbital. Since the observed changes are very small (Table 2) it is probable that either the substitution of dppe for two CO groups does not greatly affect the donor ability of the iron atom, or that the tin orbital contribution towards the iron–tin bonding orbital has large $5s$ and small $5p$ character, as an increase in the ability of the iron atom to donate

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electrons into an orbital with a small tin $5p_z$ character would not greatly affect the ^{119}Sn quadrupole splitting. This second explanation seems the most likely and supports the conclusions reached from other Mössbauer studies.[4,15,19]

The ^{119}Sn centre shift is in each case higher for the dppe complex than for the analogous dicarbonyl complex. This is as expected on the basis that substitution of dppe will result in a higher electron density on the iron atom, and that this will be transmitted to the tin atom *via* the iron–tin bond. Since this bond has a high *s*-character the *s*-electron density at the ^{119}Sn nucleus will thereby be increased.

TABLE 2

^{119}Sn Mössbauer parameters [a]

Compound	δ	Δ
$C_5H_5Fe(CO)_2SnCl_3$ [b]	1·67	1·82
$C_5H_5Fe(dppe)SnCl_3$ [c]	1·92	1·76
$C_5H_5Fe(CO)_2SnBr_3$ [b]	1·75	1·60
$C_5H_5Fe(dppe)SnBr_3$ [c]	1·99	1·60
$C_5H_5Fe(CO)_2SnMe_3$ [d]	1·41	0·46
$C_5H_5Fe(dppe)SnMe_3$ [d]	1·50	0·70
$C_5H_5Fe(CO)_2SnI_3$ [b]	1·88	1·50
$C_5H_5Fe(dppe)SnI_3$ [c]	2·26	1·53

[a] All centre shift values quoted relative to $BaSnO_3$ at 80 K. Line width at half height *ca.* 1·4 mm s^{-1}. [b] Ref. 15. [c] This work. [d] Ref. 4.

EXPERIMENTAL

Dry AnalaR solvents were used throughout and were degassed before use. All preparations were carried out under nitrogen. The light petroleum used boiled in the range 30—40°. $C_5H_5Fe(CO)_2CH_3$ [14] and $C_5H_5Fe(CO)_2$-$SnBr_3$ [20] were prepared according to literature methods. ^{57}Fe Mössbauer spectra were obtained with a ^{57}Co source in palladium and an experimental arrangement already described.[21] All centre shift values are quoted relative to sodium nitroprusside. ^{119}Sn Mössbauer spectra were obtained with a $BaSnO_3$ source and centre shift values are quoted relative to $BaSnO_3$. All spectra were fitted without constraints to Lorentzian line shapes by techniques already described.[22]

Preparations.—(*a*) $FeCl_2$(dppe). $FeCl_2$ (0·454 g, 3·6 mmol) was dissolved in acetone (30 ml) and the solution added to a solution of dppe (2·0 g) in chloroform (20 ml). After refluxing for 3 h, the white precipitate which had formed was filtered off, washed with ether, and dried in air. Yield 1·68 g (86%) (Found: C, 59·1; H, 4·9. $C_{26}H_{24}FeP_2$ requires C, 59·5; H, 4·8%).

(*b*) C_5H_5Fe(dppe)Cl,$CHCl_3$. In a typical experiment TlC_5H_5 (1·34 g, 5 mmol) and $FeCl_2$(dppe) (2·62 g, 5 mmol) were stirred in benzene (200 ml) for ½ h. The solution darkened rapidly and a precipitate of TlCl formed. After centrifuging the solution to remove this precipitate evaporation to dryness gave the crude product in *ca.* 80% yield. This was purified by chromatography on alumina ($CHCl_3$ eluant), adding diethyl ether to the resulting solution and cooling. Large black crystals of the complex were obtained overnight. Yield 70% (Found: C, 57·0; H, 4·4; Cl, 19·7. $C_{32}H_{30}ClFeP_2$ requires C, 57·0; H, 4·5; Cl, 21·0%).

(*c*) $C_5H_5Fe(dppe)SnCl_3$. C_5H_5Fe(dppe)Cl,$CHCl_3$ (0·2 g, 0·3 mmol) was refluxed with a slight molar excess of anhydrous $SnCl_2$ in thf (25 ml) for 2 h. The initially dark coloured solution became red in colour during this time and the crude product was then precipitated by addition of light petroleum to the cold solution. The red powder so obtained was recrystallised from thf–light petroleum. Yield 80% (Found: C, 50·0; H, 4·2; Cl, 15·0. $C_{31}H_{29}Cl_3FeP_2Sn$ requires C, 50·0; H, 3·9; Cl, 14·3%).

(*d*) $C_5H_5Fe(dppe)SnBr_3$. $C_5H_5Fe(dppe)SnCl_3$ (0·2 g, 0·27 mmol) prepared as above was refluxed for ½ h in 1 : 1 thf–methanol (30 ml) with a 10-fold molar excess of anhydrous $SnBr_2$. The resulting solution was partially evaporated and then cooled, giving dark red crystals of the pure product. Yield 60% (Found: C, 42·8; H, 3·2. $C_{31}H_{29}Br_3FeP_2Sn$ requires C, 42·4; H, 3·3%).

(*e*) $C_5H_5Fe(dppe)SnI_3$. C_5H_5Fe(dppe)Cl,$CHCl_3$ (1 g, 1·48 mmol) and anhydrous SnI_2 (2·5 g, 7·6 mmol) were refluxed in 1 : 2 thf–methanol (30 ml) for ½ h. The solution was filtered hot and then allowed to cool whereupon very dark green crystals of the product separated. Yield 30% (Found: C, 37·0; H, 3·0. $C_{31}H_{29}FeI_3P_2Sn$ requires C, 36·6; H, 2·9%).

(*f*) $C_5H_5Fe(dppe)SnMe_3$. Solid $C_5H_5Fe(dppe)SnCl_3$ (0·5 g, 0·67 mmol) was added in small portions to a large (10-fold) excess of MeMgI in ether solution (70 ml). A rapid reaction occurred giving an orange solution which was then hydrolysed with aqueous NH_4Cl to remove the excess of Grignard reagent. After separating the ether layer and drying it over sodium sulphate it was chromatographed on alumina. The first yellow-orange band eluted with diethyl ether was collected and the crystalline complex obtained by partial evaporation and by cooling. Yield 20% (Found: C, 60·8; H, 5·7. $C_{34}H_{38}FeP_2Sn$ requires C, 59·8; H, 5·6%).

(*g*) C_5H_5Fe(dppe)Me. A solution of C_5H_5Fe(dppe)Cl,-$CHCl_3$ in thf was added to a large (10-fold) excess of MeMgI in ether solution. After stirring for ½ h and washing with NH_4Cl aq., the ether layer was dried over Na_2SO_4. Addition of light petroleum to the partially evaporated solution gave dark red needles of the product. Yield 40% (Found: C, 71·6; H, 6·2. $C_{32}H_{32}FeP_2$ requires C, 72·0; H, 6·0%).

(*h*) C_5H_5Fe(dppe)H. C_5H_5Fe(dppe)Cl,$CHCl_3$ (0·5 g, 0·74 mmol) and $NaBH_4$ (0·5 g, 13·5 mmol) were stirred in thf (50 ml) for ½ h. The yellow solution so obtained was centrifuged and evaporated to give a brown oil. This was extracted with hexane and cooled to −20 °C to give yellow crystals of C_5H_5Fe(dppe)H (200 mg). Yield 50% (Found: C, 71·6; H, 5·8; P, 10·8. $C_{31}H_{30}FeP_2$ requires C, 71·6; H, 5·8; P, 11·9%).

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