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Preliminary communication

A STABLE CATIONIC COMPLEX OF IRON CONTAINING THE PHENYLVINYLIDENE LIGAND

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Summary

The cationic complex *trans*-$[FeCl(C{=}CHPh)(depe)_2]^+$ (depe = bis(diethylphosphino)ethane has been prepared by interaction of *trans*-$[FeCl_2(depe)_2]$ with phenylacetylene in methanol solution in the presence of NaX (X = BPh_4 or PF_6).

The reaction of a methanolic solution of *trans*-$[PtCl(CH_3)L_2]$ (L = $P(CH_3)_2$-C_6H_5 or $As(CH_3)_3$) with monoalkyl- or monoaryl-acetylenes in the presence of $AgPF_6$ gives methoxy—carbene complexes of the type *trans*-$[PtCH_3\{C(OCH_3)CH_2R\}L_2]$ [1]. This reaction has been postulated to proceed via a vinylidene intermediate of the type $Pt{-}C^+{=}CHR$ but at the time this suggestion was made no stable vinylidene complex of this type was known. Recently, however, a manganese complex containing a phenylvinylidene ligand has been described [2]. We now report the synthesis and some spectroscopic characteristics of a stable cationic phenylvinylidene complex of iron.

Reaction of phenylacetylene with a methanol solution of *trans*-$[FeCl_2(depe)_2]$ under argon at 20°C for 1 hour followed by addition of $NaPF_6$ in methanol gave the dark green salt *trans*-$[FeCl(C_2HPh)(depe)_2]PF_6$ (depe = 1,2 bis(diethylphosphino)ethane) which was recrystallised from methanol. Found: C, 44.9; H, 7.0; P, 19.9. $C_{28}H_{54}P_5F_6ClFe$ calcd.: C, 44.9; H, 7.2; P, 20.6%. The corresponding BPh_4^- salt was also prepared by addition of $NaBPh_4$ and recrystallisation of the precipitated complex from acetone. Both compounds are stable in dry air and conductivity measurements on the BPh_4^- salt in nitromethane indicate that it is a 1:1 electrolyte.

The ^1H NMR spectrum of the tetraphenylborate salt (CH_2Cl_2 solution) shows absorptions at τ 3.0 ppm, m, 25H (aromatic protons), τ 8—9 ppm, m, 48H (depe protons) and 5.08 ppm, q, 1H (J(H—P) 4 Hz). This last resonance we assign to the olefinic hydrogen atom on the vinylidene ligand bonded as in structure I. The

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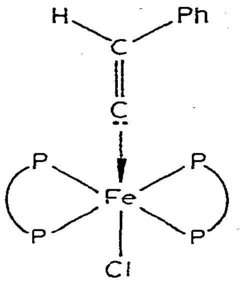
equivalent coupling to the four phosphorus atoms indicates that there is free rotation about the Fe—C bond.



The IR spectra of the two salts (Nujol mulls) show no bands in the 2000 cm^{-1} region attributable to ν(C≡C). However, four bands of medium intensity appear at 1609, 1595, 1588 and 1572 cm^{-1} which are not present in the IR spectra of other complexes of the type *trans*-[FeClL(depe)$_2$]$^+$ [3] and we assign these bands to coupled ν(C=C) modes within the phenylvinylidene ligand.

The Mössbauer parameters for *trans*-[FeCl(C=CHPh)(depe)$_2$]$^+$ are given in Table 1 together with those for two related complexes.

TABLE 1

MÖSSBAUER PARAMETERS FOR *trans*-[FeCl(C=CHPh)(depe)$_2$]$^+$ AND TWO RELATED COMPLEXES

Complex	δ	Δ	Ref.
trans-[FeCl(C=CHPh)(depe)$_2$]$^+$	0.25	1.22	This work
trans-[FeCl(CO)(dmpe)$_2$]$^{+a}$	0.33	0.88	3
trans-[FeCl(NO)(depe)$_2$]$^{2+}$	0.26	2.15	3

^{a}dmpe = $(CH_3)_2PCH_2CH_2P(CH_3)_2$.

The low value of δ for the vinylidene complex indicates that (C=CHPh) is either a good σ-electron donor or a good π-acceptor ligand, comparable to NO$^+$ in its effect on the *s*-electron density at the ^{57}Fe nucleus. Making the reasonable assumption that the sign of Δ is positive [4] it may be concluded that (C=CHPh) is a relatively good π-acceptor ligand, although not as good as NO$^+$. The validity of the conclusion is supported by the X-ray structure analysis for [η-C_5H_5Mn(CO)$_2$-(C=CHPh)] which shows that the Mn—C bond length is much shorter than a Mn—C single bond and even shorter than the Mn—C (carbene) bond in [η-C_5H_5-Mn(CO)$_2$ {C(Ph)COPh}].

The reactions of the iron complex are under study. It is noteworthy, that it shows no tendency to react with alcohols to give alkoxycarbene complexes.

References

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