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INSERTION OF GROUP IVB METAL DIHALIDES INTO IRON-CARBON SIGMA BONDS[‡]

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Summary

The insertion reaction of $GeCl_2$, $SnCl_2$ and $SnBr_2$ into the iron-carbon sigma bond in the compounds $Cp(CO)_2FeR$ (R = methyl, ethyl, n-propyl, p-methoxybenzyl, benzyl and p-trifluoromethylbenzyl), to yield complexes with the Group IV metal bound to iron, is a radical chain process. A small substituent effect is observed in all cases for the benzyl series, the reaction being favoured by increasing electron donating ability of the *para* substituent. No clear reactivity trend is noted for the other alkyl complexes.

Introduction

Tin(II) and germanium(II) halides undergo numerous oxidative-addition reactions, in which they formally insert into

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transition metal-transition metal and transition metal-halogen bonds to produce compounds containing the Group IVB metal bound to the transition metal[1]. A few cases of insertion into transition metal-carbon σ-bonds have also been noted, but generally the reactions have been less widely explored. Both tin(II) chloride[2] and germanium(II) chloride[3], as its dioxan adduct, insert, in tetrahydrofuran (THF) solution, into the iron-carbon bond in the alkyl compounds $Cp(CO)_2FeR$ to give $Cp(CO)_2FeMX_2R$ species. Limited details of relative reativities are available; for tin(II) chloride, the rate of insertion with $Cp(CO)_2FeMe$ was found to be much greater than with $Cp(CO)_2FeEt$, but the opposite order was observed for the germanium(II) chloride reactions. The complete reactivity order for the latter case,

$$^{i}Pr > {}^{n}Pr > Et > Me > CH_2Ph$$

coupled with the non-reaction of the compounds $Cp(CO)_2FeCF_3$ and $Cp(CO)_2FeC_6F_5$, was interpreted[3] as being in accord with the electrophilic nature of the $GeCl_2$.dioxan complex, the attack of which on the Fe-C bond was expected to be faster, the higher the electron density on the transition metal atom. More recently, a similar reaction of tin(II) chloride with some $Cp(CO)_2Fe(\sigma\text{-allyl})$ systems has been noted[4]. Insertion reactions of a tin(II) alkyl, $Sn[CH(SiMe_3)_2]_2$, with $Cp(CO)_2FeMe$ and $Cp(CO)_3MoMe$, have also been reported[5].

In view of the substantial recent interest in the behaviour of the transition metal-carbon σ-bond in a variety of insertion processes[6], we were encouraged to study further the apparent reactivity differences in the $Cp(CO)_2FeR$ systems. We have attempted to extend the scope of the reaction, and have collected rate data for para-substituted benzyl iron complexes in the hope of achieving a more reasonable separation of electronic and steric factors in reactivity. The apparent electrophilic character of $GeCl_2$.dioxan was also of interest to us in view of several recent reports of Lewis acidity of tin(II) and germanium(II) compounds in complexes such as $\{[(Me_3Si)_2CH]_2Sn\}Mo(CO)_5$ [7], $Cl_2GeCr(CO)_5$ [8], $Cp_2SnMo(CO)_5$ [9], and $[{}^tBu_2Sn(py)]Cr(CO)_5$ [10].

Results and Discussion

The reactions of $GeCl_2$.dioxan, and anhydrous $SnCl_2$ and $SnBr_2$, with various $Cp(CO)_2FeR$ compounds were studied in THF and methanol solutions which were approximately 0.35 M in both reagents, and monitored by observing changes in the Cp region of the ^1H NMR spectrum. The reactions were significantly promoted even by weak sunlight, showed, in some cases, significant induction periods, and occasionally proceeded erratically. These observations suggested the involvement of free-radical reaction pathways, a possibility reinforced by the complete inhibition of reaction on the addition of small amounts of the radical scavenger, 1,1-diphenyl-2-picrylhydrazyl. Although the usual precautions were taken to exclude light, oxygen and water in all reactions, it is suspected that the observed variations in reactivity may be associated with the presence of traces of these materials. In view of these problems, the rate data obtained were of poor quality, but did suggest that the reaction was effectively first order, beyond the induction periods, in both $Cp(CO)_2FeR$ and the metal(II) halide. Approximate average rate constants are calculated on this basis. Large variations (up to 30%) were observed for similar experiments carried out under apparently comparable conditions and the rate constants must therefore be interpreted cautiously. However, we believe that some gross features of reactivity are still apparent.

The insertion reactions of $GeCl_2$.dioxan with $Cp(CO)_2FeR$, (R = methyl, ethyl, n-propyl, p-methoxybenzyl, benzyl and p-trifluoromethylbenzyl), proceed easily under mild conditions in THF solutions; for example, at 65°C, the dark reaction of $Cp(CO)_2FeCH_2Ph$ is essentially complete within two hours. The reactions appear to be significantly faster than previously reported[3] but a strict comparison is impossible as, while Nesmeyanov et al. quote relative reactivities, no rate data are presented, and the arguments seem to rely on reaction times and yields, sometimes in different solvent mixtures and at different temperatures. The reactions were fast even at 40°C, with half-lives of several hours, but measurements at this temperature were bedevilled by variable and sometimes lengthy (1-2 hour) induction periods. Accordingly, rates (for the dark reactions) were measured at 56° (induction periods around 10 minutes) and at 65°. At both these temperatures, a reproducible rate order for the para-substituted benzyl complexes, p-MeO ($k(65°) \sim 4\times10^{-3}$ litre $mole^{-1}$ sec^{-1}; $k(56°) \sim 1\times10^{-3}$) > H ($k(65°) \sim 2\times10^{-3}$; $k(56°) \sim 5\times10^{-4}$) > p-$CF_3$ ($k(65°) \sim 4\times10^{-5}$; $k(56°) \sim 1\times10^{-5}$), was observed. The trend is clearly in line with the order of electron-donating ability of the para substituents, and a similar conclusion, that of enhanced attack on the Fe-C bond the greater the electron density in it, to that advanced previously[3], can be drawn. We find no pronounced trend for the alkyl series where R = Me, Et and ^{n}Pr. All the reactions are faster even than for the p-methoxybenzyl system, and, at 56°C, are probably in the order Et (reaction complete within 10 minutes) > ^{n}Pr ($k \sim 3\times10^{-3}$ litre mole^{-1} sec^{-1}) > Me($k \sim 2\times10^{-3}$).

The insertion reactions are essentially clean; a small amount ($\sim$ 2%) of $Cp(CO)_2FeGeCl_3$ is always formed, but we cannot confirm the earlier observation[3] that its amount increases with increase in the inductive effect of the alkyl ligand. Rather, we believe that its formation is a consequence of side reactions induced by water and oxygen impurities, and by small amounts of Ge(IV) species in the $GeCl_2$.dioxan.

The corresponding dark insertion reactions of anhydrous $SnCl_2$ in THF at 65°C are much slower. Only very small amounts ($\sim$ 1-2%) of $Cp(CO)_2FeSnCl_3$ are formed as by-products. Rates were somewhat less variable in this system and the same reactivity order in the benzyl series, pMeO ($k \sim 2\times10^{-4}$ litre mole^{-1} sec^{-1}) > H($k \sim 8\times10^{-5}$) > p-CF_3 ($k \sim 7\times10^{-6}$), was observed. Relative to the benzyl compounds, the alkyl iron compounds (Me, $k \sim 2\times10^{-5}$; Et, $k \sim 2\times10^{-6}$) were, for $SnCl_2$, significantly less reactive than with $GeCl_2$. With $Cp(CO)_2FeEt$, a side reaction yielding $[Cp(CO)_2Fe]_2SnCl_2$, is significant at 65° and 78°, and might involve the slow decomposition of the iron-ethyl compound to the hydride, followed by its further decomposition to $[Cp(CO)_2Fe]_2$. $SnCl_2$ insertion into the latter is known to be a facile process[11].

Within experimental error, we were unable to distinguish any clear differences between the reactivity of anhydrous $SnCl_2$ and $SnBr_2$. The p-methoxybenzyl iron compound ($k \sim 2\times10^{-4}$ litre mole^{-1} sec^{-1}), with $SnBr_2$ in THF at 65°C, again reacted more quickly than the benzyl compound ($k \sim 7\times10^{-5}$), but the rates of reaction with $Cp(CO)_2FeMe$ ($k \sim 3\times10^{-6}$) and $Cp(CO)_2FeEt$ ($k \sim 3\times10^{-6}$) were comparable. The results with anhydrous $SnBr_2$ contrast to our earlier ones involving $SnBr_2.2H_2O$ where no insertion was observed with $Cp(CO)_2FeMe$[2]. The non-reaction is probably related to the low solubility of the dihydrate in THF, and the small amounts of $Cp(CO)_2FeBr$, and later $Cp(CO)_2FeSnBr_3$, which are formed, in this case, could arise from a hydrolysis reaction leading to the cleavage of the iron-methyl bond by HBr. In this regard, we have recently noted that the use of both $SnCl_2.2H_2O$ and $SnBr_2.2H_2O$ causes significant side reactions to occur in the insertion of the tin(II) halide into the metal-metal bonds of $[Cp(CO)_2Fe]_2$ and $[Cp(CO)_3Mo]_2$[11]. Interestingly, $SnCl_2.2H_2O$ inserts normally into $Cp(CO)_2FeMe$[2].

The $SnCl_2$ insertion reactions also proceed cleanly at 65°C in d^1-methanol solution at rates not significantly different from those in THF. The same reactivity order, p-methoxybenzyl ($k \sim 2\times10^{-4}$ litre mole^{-1} sec^{-1}) > benzyl ($k \sim 1\times10^{-4}$), was observed. Reactions of $GeCl_2$.dioxan could not be studied because of its immediate reaction with the solvent[12]. The addition of 5 mole % of 1,1-diphenyl-2-picrylhydrazyl completely stopped the $SnCl_2$ insertion reactions in methanol, and, as in THF, the only reaction (by I.R.) was slight (<5%) formation of $Cp(CO)_2FeCl$ in the initial stages which was slowly converted, on long reflux, to $Cp(CO)_2FeSnCl_3$.

The effect of the radical inhibitor on all the systems studied is such as to suggest a radical chain sequence in the reaction path. Even much smaller amounts (1%) stopped the reaction, but in this case insertion commenced after long (~24 hours) induction delays. In view of these observations, an attempt was made to "spin-trap" possible radical species in the $SnX_2/Cp(CO)_2FeR$ systems, however the reactions proved far too slow for this technique and no spin-adducts were detected[13].

Conclusions

The rates of insertion of $GeCl_2$.dioxan and the tin(II) halides of the p-substituted benzyl iron complexes show a clear enhancement in reactivity with electron donating substituents. Variable trends were observed for other simple alkyl substituents, for which differing steric factors may also be involved. The relatively small substituent effects in the benzyl series are consistent with the involvement of free radicals in the reaction pathway, probably in a chain process. The greater ease of oxidative-addition to $GeCl_2$ was not unexpected, but the reason for the close correspondence of the reactivity of $SnCl_2$ and $SnBr_2$ is not immediately clear. The issue is complicated by uncertainty as to the solution species for these compounds: moieties such as $[ClSnL]^+$ and $[SnCl_3]^-$ have been proposed to exist in donor solvents[14]. No evidence was found for the intermediacy, or otherwise, of Lewis acid-type complexes of the MX_2 compounds in the insertion reactions.

Experimental

All handling operations were done under high purity nitrogen using conventional Schlenk techniques. THF was dried over CaH_2 and methanol over Mg, and both were freshly distilled under nitrogen before use. Tin(II) chloride (Ajax) and tin(II) bromide (ROC-RIC) were dried under vacuum and stored under nitrogen. $GeCl_2$.dioxan was prepared by the literature method[15]. The several $Cp(CO)_2FeR$ derivatives were prepared by the usual reactions of $[Cp(CO)_2Fe]^-$ with alkyl halides. Kinetic data were collected by monitoring the peak heights of reactants (e.g. $\tau(Cp) = 5.57$ for $Cp(CO)_2FeMe$ in THF) and products (e.g. $\tau(Cp) = 5.37$ for $Cp(CO)_2FeSnCl_2Me$ in THF) on a Varian EM-360 spectrometer. Samples were heated, in sealed tubes, in the vapours of refluxing MeOH (65°C), acetone (56°C), or methylene chloride (40°C), as appropriate. Infrared spectra were recorded on a PE457 spectrophotometer.

Preparative scale reactions were done for $Cp(CO)_2FeCH_2Ph$ with both $SnCl_2$ and $SnBr_2$, and the products, which were taken as representative of the new series of derivatives, characterised. Microanalyses were carried out by Mr. J. Kent of this Department.

$Cp(CO)_2Fe(SnCl_2CH_2Ph)$	Found:	C, 36.5; H, 2.7; Cl, 15.8%.
	Calculated:	C, 36.8; H, 2.6; Cl, 15.5%.
$Cp(CO)_2Fe(SnBr_2CH_2Ph)$	Found:	C, 30.6; H, 2.3; Br, 29.0%.
	Calculated:	C, 30.8; H, 2.2; Br, 29.3%.

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References

1 See E.H. Brooks and R.J. Cross, Organometal. Chem. Rev. A, 6 (1970), 227.

2 B.J. Cole, J.D. Cotton and D. McWilliam, J. Organometal. Chem., 64 (1974) 223.

3 A.N. Nesmeyanov, N.E. Kolobova, K.S. Anisimov and F.S. Denisov, Proc. Acad. Sci. U.S.S.R., 192 (1970) 813.

4 C.V. Magatti and W.P. Giering, J. Organometal. Chem., 73 (1974) 85.

5 J.D. Cotton, P.J. Davidson and M.F. Lappert, J. Chem. Soc. Dalton, (1976) 2275.

6 A. Wojcicki, Advan. Organometal. Chem., 11 (1973) 87; ibid., 12 (1974) 31.

7 J.D. Cotton, P.J. Davidson, D.E. Goldberg, M.F. Lappert and K.M. Thomas, J. Chem. Soc. Chem. Commun., 1974, 893.

8 D. Uhlig, H. Behrens and E. Lindner, Z. Anorg. Allgem. Chem., 401 (1973) 233.

9 A.B. Cornwell, P.G. Harrison and J.A. Richards, J. Organometal. Chem., 108 (1976) 47.

10 M.D. Brice and F.A. Cotton, J. Amer. Chem. Soc., 95 (1973) 4529.

11 J.D. Cotton and A.M. Trewin, J. Organometal. Chem., 117 (1976) C7.

12 J. Satgé, M. Massol and P. Rivière, J. Organometal. Chem., 56 (1973) 1.

13 J. MacQuitty, personal communication.

14 T.N. Sumarokova and D.E. Surpina, Izv. Akad. Nauk. Kaz. SSR. Ser. Khim., (1969) 16; Chem. Abstr., 72 (1969) 27926e.

15 S.P. Kolesnikov, V.I. Shiryaev and O.M. Nefedov, Izv. Akad. Nauk. SSSR., Ser. Khim., (1966) 584.