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# PHOTOCHEMICALLY INDUCED INSERTION OF ALKYNES INTO THE METAL—METAL BOND OF $[FeX(CO)_3]_2$ COMPLEXES ($X = SCH_3, SC_6H_5, P(CH_3)_2$)

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## Summary

It is shown that alkynes, such as $CF_3C{\equiv}CCF_3$ and $CH_3OOCC{\equiv}CCOOCH_3$, which contain strongly electron-attracting groups, undergo insertion into the metal—metal bond of $[FeX(CO)_3]_2$ complexes ($X = SCH_3, SC_6H_5, P(CH_3)_2$) under UV irradiation. The reactions of the products with trimethylphosphine are also described.

In their complexes, alkynes frequently occupy the $\mu$-bridging position between two metal atoms [1]. In most cases the C—C bond is perpendicular to the metal—metal axis and there is $\pi$-interaction between the alkyne and each metal atom. There are also cases in which the C—C bond and the metal—metal axis are parallel and the alkyne is $\sigma$-bonded to two metal atoms, e.g. $(PPh_3)_2Au_2(CF_3C_2CF_3)$ [2], $(PPh_3)_2Ir_2(NO)_2(CF_3C_2CF_3)$ [3], $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ [4] and $Fe_2(CO)_6(SCF_3)_2(CF_3C_2CF_3)$ [5,6]. In the last case Davidson and Sharp showed that insertion into $[FeSCF_3(CO)_3]_2$ occurred thermally with hexafluorobut-2-yne and photochemically with trifluoropropyne [6]. As a perfluoroalkyl group bonded to the bridging atom is likely to have a significant influence in these complexes, in particular through metal—metal bond lengthening [7], we have undertaken a more general study of the insertion of alkyne into $Fe_2X_2(CO)_6$ complexes when $X = SCH_3$, $SC_6H_5$ and $P(CH_3)_2$ in order to determine the influence of the bridging group on the reactivity of the dinuclear complexes.

## Results and discussion

There is no thermal reaction below 120°C between the $Fe_2X_2(CO)_6$ compounds and the activated alkynes, and this observation confirms the special

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TABLE 1

$\nu$(CO) AND $\nu$(C=C) of $[FeX(CO)_3]_2RC{\equiv}CR$ COMPLEXES

| Complex | $\nu(C{\equiv}O)$ [a] | $\nu$(C=C) [b] |
|---|---|---|
| $[FeSCH_3(CO)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | 2093vw 2075vs 2033s 2021s 2018(sh) | 1516 |
| $[FeSC_6H_5(CO)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | 2095vw 2079vs 2038s 2029s 2019(sh) | 1528 |
| $[FeSCH_3(CO)_3]_2CF_3C{\equiv}CCF_3$ | 2097vw 2081vs 2073(sh) 2044(sh) 2040s 2030s | 1522 |
| $[FeSC_6H_5(CO)_3]_2CF_3C{\equiv}CCF_3$ | 2097vw 2083vs 2078(sh) 2042s 2038s | 1520 |
| $[FeP(CH_3)_2(CO)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | 2071vw 2057vs 2015s 1992s | 1508 |
| $[FeP(CH_3)_2(CO)_3]_2CF_3C{\equiv}CCF_3$ | 2061vs 2022s 2001s 1990(sh) | 1495 |

[a] In $cm^{-1}$ measured in hexadecane. [b] In $cm^{-1}$ measured in KBr pellets.

behaviour of $SCF_3$ bridges. Under irradiation of the benzene solution from medium pressure mercury vapour lamp, insertion of $RC{\equiv}CR$ occurs when R is an electron-attracting group as $CF_3$ or $COOCH_3$. When R = $C_6H_5$ or H no insertion is observed. The nature of the bridges has an influence on the rate of the reactions, the reactions being slower with $P(CH_3)_2$ than with SR bridges. The greater steric crowding around the metal—metal bond in the case of $[Fe(CO)_3P(CH_3)_2]_2$ compounds is probably one factor in this behaviour.

## *Assignment of the configuration*

Infrared spectra in the $\nu$(CO) stretching region of the complexes $[FeX(CO)_3]_2RC{\equiv}CR$ are shown in Table 1. They are very similar to the infrared spectra of the $[FeSCF_3(CO)_3]_2RC{\equiv}CR$ compounds described by Davidson and Sharp [6]. We conclude that the structure of $[FeX(CO)_3]_2RC{\equiv}CR$ is very similar to that of $[FeSCF_3(CO)_3]_2CF_3C{\equiv}CCF_3$ [5], i.e. the alkyne is $\sigma$-bonded to the two iron atoms. As in the case of $[FeSCF_3(CO)_3]_2RC{\equiv}CR$ all these compounds show a band of moderate intensity in the 1520 $cm^{-1}$ region attributable to the $\nu$(C=C)

TABLE 2

PROTON AND FLUORINE NMR DATA FOR $[FeX(CO)_3]_2RC{\equiv}CR$ COMPLEXES

| Complex | $^1H$ NMR [a] | | | | $^{19}F$ NMR [b] |
|---|---|---|---|---|---|
| | $\delta(OCH_3)$ | $\delta(SCH_3)$ | $\delta(PCH_3)$ | $J(PCH_3)$ [c] | $\delta(CF_3)$ |
| $[FeSCH_3(CO)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | −3.76 | −2.43, −1.71 $I = 4$<br>−1.88 $I = 1$ | | | |
| $[FeSC_6H_5(CO)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | −3.75 | | | | |
| $[FeSCH_3(CO)_3]_2CF_3C{\equiv}CCF_3$ | | −1.41, −1.68 $I = 5$<br>−1.85 $I = 1$ | | | −31.5 |
| $[FeSC_6H_5(CO)_3]_2CF_3C{\equiv}CCF_3$ | | | | | −32.5 |
| $[FeP(CH_3)_2(CO)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | −3.71 | | −1.63<br>−1.92 | 5.8<br>5.1 | |
| $[FeP(CH_3)_2(CO)_3]_2CF_3C{\equiv}CCF_3$ | | | −1.60<br>−1.91 | 5.6<br>5.0 | −31 |

[a] In ppm from TMS as internal reference in $CH_2Cl_2$. [b] In ppm from $CF_3COOH$ as external reeference in $CH_2Cl_2$. [c] In Hz (1.2.1.triplets due to $J(PP)$ coupling).

TABLE 3

$\nu$(CO) AND $\nu$(C=C) FOR $[FeX(CO)_2P(CH_3)_3]_2RC{\equiv}CR$ COMPLEXES

| Complex | $\nu$(C≡O) [a] | $\nu$(C=C) [b] |
|---|---|---|
| $[FeSCH_3(CO)_2P(CH_3)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | 2016m 2002s 1958s | 1512 |
| $[FeSC_6H_5(CO)_2P(CH_3)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | 2025m 2010s 1964s | 1512 |
| $[FeSCH_3(CO)_2P(CH_3)_3]_2CF_3C{\equiv}CCF_3$ | 2024m 2009s 1966s | 1512 |
| $[FeSC_6H_5(CO)_2P(CH_3)_3]_2CF_3C{\equiv}CCF_3$ | 2029m 2024s 1969s | 1512 |

[a] In cm$^{-1}$ measured in $CH_2Cl_2$. [b] In cm$^{-1}$ measured in KBr pellets.

stretch. This band occurs at lower frequencies in the case of $P(CH_3)_2$ bridges.

Table 2 lists the proton NMR data for the $SCH_3$ and $OCH_3$ groups and the fluorine NMR data for the $CF_3$ group of $CF_3C{\equiv}CCF_3$. It appears that the main difference between the complexes studied and the $[FeSCF_3(CO)_3]_2RC{\equiv}CR$ compounds is the *syn*/*anti* isomer ratio: with the $SCF_3$ bridge the *syn*-isomer is the major component but in the $SCH_3$ case the *anti* isomer is the predominant form.

*Action of trimethylphosphine*

At room temperature $P(CH_3)_3$ displaces two CO groups of $[FeX(CO)_3]_2RC{\equiv}CR$ complexes for X = $SCH_3$ or $SC_6H_5$. With X = $P(CH_3)_2$ no reaction occurs at this temperature. As in reaction of $P(C_6H_5)_3$ with $[FeSCF_3(CO)_3]_2RC{\equiv}CR$ compounds [6], no monosubstituted compound is detected; when the ratio $P(CH_3)_3/[FeX(CO)_3]_2RC{\equiv}CR$ is 1 only a mixture of disubstituted product and starting material is detected. It is possible to get the same products by ultraviolet irradiation of a solution of $[Fe(CO)_2P(CH_3)_3SR]_2$ complexes and the alkynes.

The $\nu$(CO) stretching frequencies of the compounds and the $\nu$(C=C) frequencies are listed in Table 3. All the compounds have three infrared active bands, from which we conclude that they have $C_{2v}$ symmetry with the two phosphines *trans* to the bridging olefin.

The proton NMR data (Table 4) confirm that there is only one type of phosphine ligand; there is also one $SCH_3$ resonance, and the $SCH_2$ groups are in *syn* dispositions. It is not possible to say if they are in the axial position, as in $[FeSCF_3(CO)_3]_2CF_3C{\equiv}CCF_3$ complexes [5], because in our case the two phosphines increase the steric crowding in this part of the molecule.

It is noteworthy that substitution of two CO by two $P(CH_3)_3$ ligands induces a slight lowering of the $\nu$(C=C) stretching frequencies.

TABLE 4

PROTON NMR DATA FOR $[FeX(CO)_2P(CH_3)_3]_2RC{\equiv}CR$ COMPLEXES

| Complex | $\delta(OCH_3)$ [a] | $\delta(SCH_3)$ [a] | $\delta(PCH_3)$ [a] | $J$(PCH) [b] |
|---|---|---|---|---|
| $[FeSCH_3(CO)_2P(CH_3)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | −3.68 | −1.75 | −1.45 | 8.4 |
| $[FeSC_6H_5(CO)_2P(CH_3)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | −3.70 | | −1.50 | 8.5 |
| $[FeSCH_3(CO)_2P(CH_3)_3]_2CF_3C{\equiv}CCF_3$ | | −1.75 | −1.48 | 8.6 |
| $[FeSC_6H_5(CO)_2P(CH_3)_3]_2CF_3C{\equiv}CCF_3$ | | | −1.55 | 8.6 |

[a] In ppm relative to internal TMS in $CH_2Cl_2$. [b] In Hz (signals as doublets).

TABLE 5

PHYSICAL AND ANALYTICAL DATA OF $[FeX(CO)_3]_2RC{\equiv}CR$ AND $[FeX(CO)_2P(CH_3)_3]_2RC{\equiv}CR$ COMPLEXES

| Complex | Irradiation time (h) | Yield (%) | Colour | M.p. (°C) | Analysis found (calcd.) (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | F | P |
| $[FeSCH_3(CO)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | 1 | 70 | yellow | 100 (dec) | 32,75<br>(32,55) | 2,49<br>(2,32) | | |
| $[FeSCH_3(CO)_3]_2CF_3C{\equiv}CCF_3$ | 2 | 50 | yellow | 135 (dec) | 26,87<br>(26,86) | 1,15<br>(1,11) | 20,98<br>(21,27) | |
| $[FeSC_6H_5(CO)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | 1 | 75 | brown | 115 (dec) | 44,79<br>(45,00) | 2,62<br>(2,50) | | |
| $[FeSC_6H_5(CO)_3]_2CF_3C{\equiv}CCF_3$ | 2 | 45 | brown | 103 (dec.) | 40,12<br>(40,00) | 1,74<br>(1,51) | 17,06<br>(17,27) | |
| $[FeP(CH_3)_2(CO)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | 20 | 40 | pale yellow | 157 | 35,45<br>(35,29) | 3,22<br>(3,30) | 11,23<br>(11,39) | |
| $[FeP(CH_3)_2(CO)_3]_2CF_3C{\equiv}CCF_3$ | 30 | 30 | pale yellow | 180 | 29,85<br>(29,78) | 2,18<br>(2,13) | 20,46<br>(20,21) | 10,87<br>(10,99) |
| $[FeSCH_3(CO)_2P(CH_3)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | | 90 | pale yellow | 186 (dec) | 35,47<br>(35,29) | 4,99<br>(4,90) | | 10,15<br>(10,13) |
| $[FeSCH_3(CO)_2P(CH_3)_3]_2CF_3C{\equiv}CCF_3$ | | 90 | pale yellow | 86 | 30,48<br>(30,37) | 3,86<br>(3,79) | 18,34<br>(18,02) | 9,85<br>(9,81) |
| $[FeSC_6H_5(CO)_2P(CH_3)_3]_2CH_3COOC{\equiv}CCOOCH_3$ | | 85 | yellow | 142 | 45,43<br>(45,65) | 4,69<br>(4,61) | | 8,52<br>(8,42) |
| $[FeSC_6H_5(CO)_2P(CH_3)_3]_2CF_3C{\equiv}CCF_3$ | | 80 | yellow | 168 (dec) | 41,27<br>(41,25) | 3,79<br>(3,70) | 14,95<br>(15,08) | 8,34<br>(8,20) |

## Experimental

Infrared spectra were recorded on a Perkin—Elmer 225. Proton NMR spectra have been run on Varian A60A and fluorine NMR spectra on a Perkin—Elmer R10. $[FeSCH_3(CO)_3]_2$ was purchased from Pressure Co. $[FeSC_6H_5(CO)_3]_2$ [8] and $[FeP(CH_3)_2(CO)_3]_2$ [9] were prepared by published methods. The alkyne $CH_3OOCC{\equiv}CCOOCH_3$ (Fluka) and $CF_3C{\equiv}CCF_3$ (Pierce chemical Company) were of commercial origin and used without purification.

In a typical reaction 0.2 g of complex and slight excess of the acetylene in benzene solution were allowed to react under nitrogen, in an open system in the case of $CH_3OOCC{\equiv}CCOOCH_3$ and in a vessel fitted with a Teflon stopcock in the case of $CF_3C{\equiv}CCF_3$.

The solutions were irradiated by a water-cooled 150 W Original Hanau TQ 150 mercury vapor lamp at approximately 10 cm. The reactions were monitored by infrared spectroscopy. After the end of the reaction the solutions were filtered, the benzene was evaporated off and the solid was recrystallized from toluene/pentane (1/1). Physical constants, reaction times, yields, and analytical data are listed in Table 5.

## References

1 R.S. Dickson and P.J. Fraser, Advan. Organometal. Chem., 12 (1974) 323.
2 C.J. Gilmore and P. Woodward, Chem. Commun., (1971) 1233.
3 J. Clemens, M. Green, Ming. Cheng Kuo, C.J. Fritchie, J.T. Magne, and F.G.A. Stone, Chem. Commun., (1972) 53.
4 R.S. Dickson, H.P. Kirsch and D.J. Lloyd, J. Organometal. Chem., 101 (1975) C48.
5 J.L. Davidson, W. Harrison, D.W.A. Sharp and G.A. Sim, J. Organometal. Chem., 46 (1972) C47.
6 J.L. Davidson and D.W.A. Sharp, J. Chem. Soc. Dalton, (1975) 2283.
7 W. Clegg, Inorg. Chem., 15 (1976) 1609.
8 W. Hieber and P. Spacu, Z. Anorg. Allg. Chem., 233 (1937) 353.
9 R.G. Hayter, Inorg. Chem., 3 (1964) 711.