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σ,π-BINUCLEAR COMPLEXES OF TRANSITION METALS COORDINATED TO THE MONOOLEFIN

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SUMMARY

σ-Vinyl derivatives of iron, tungsten, or rhenium react with iron nonacarbonyl to produce σ,π-binuclear complexes of the metals in which the presence of metal–metal bonds is very dependent on the nature of the metal. That the formation of the complexes containing a metal–metal bond does not necessarily involve the presence of an electron-withdrawing group attached to the vinyl ligand has been demonstrated for the σ-vinyl derivatives of iron, although it has been shown that for such bonding to be observed the double bond in the σ-derivative should be adjacent to the iron.

INTRODUCTION

The rapid development of the chemistry of complex compounds has clearly demonstrated that an organic ligand coordinated to a transition metal atom behaves in a very different manner from the free ligand. Thus, olefins possessing a high electron density at their double bonds and therefore capable of interacting only with electrophiles, are readily attacked by nucleophiles when coordinated at Pd^{II} or Pt^{II} (ref. 1). The behaviour of a ligand coordinated to two metal atoms would be expected to be even more modified. Such binuclear complexes, however, have been described only occasionally, and even then they usually contain one ligand bonded to two identical atoms of the same transition metal. We were interested, therefore, in the study of the directed synthesis of such binuclear complexes in which atoms of a metal would be successively coordinated to one and the same ligand. The simplest model of such a complex might be a transition metal binuclear complex containing a σ- and π-bonded monoolefin. Such complexes have been obtained through the reaction of iron carbonyls with the σ-vinyl derivatives of transition metals. The influence of spatial and electronic factors on the reaction path and on the properties and structures of the compounds formed has also been studied.

RESULTS AND DISCUSSION

The σ-vinyl derivatives having a strong electron acceptor, *e.g.* acyl, adjacent to the double bond have been used as starting materials. Such an arrangement is known[2] to diminish π*-orbital energy, and hence the stability of the σ-compound itself would be expected to be enhanced while at the same time the formation of the π-complex might be favoured.

Nucleophilic substitution of the chlorine in *trans*-2-chlorovinyl ketones by the transition metal anion has been used to synthesize the corresponding σ-2-acylvinyl derivatives.

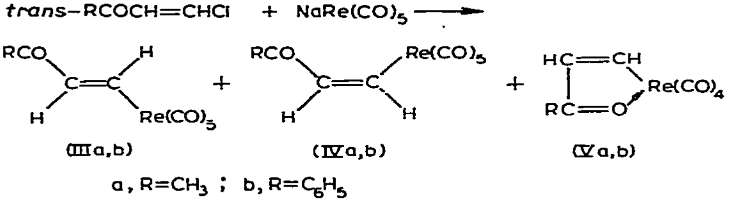
$$RCOCH{=}CHCl + NaM(CO)_nC_5H_5 \rightarrow RCOCH{=}CHM(CO)_nC_5H_5$$

(Ia, b; IIa, b, c)

(I) $M{=}Fe, n{=}2$; (II) $M{=}W, n{=}3$

a, $R{=}CH_3$; b, $R{=}C_6H_5$; c, $R{=}p\text{-}BrC_6H_4$

Unlike the Fe- or W-containing anions which only yield *trans*-$RCOCH{=}CHM(CO)_nC_5H_5$ as the sole products of their reactions with *trans*-2-chlorovinyl ketones[3,4], the rhenium pentacarbonyl anion produces a mixture containing *cis* and *trans* isomers of the σ-complex $RCOCH{=}CHRe(CO)_5$ (III), (IV) and the compound (V), in which the keto group is coordinated.



Thus, if formation of stereoisomers from the reaction involving $[Re(CO)_5]^-$ is assumed to be governed by the usual mechanism which describes the substitution of a nucleophile for a halogen in 2-chlorovinyl ketones[5,6], then the formation of the *cis*- and *trans*-$RCOCH{=}CHRe(CO)_5$ mixture may be related to the greater stability of the carbanion intermediate $R\bar{COCH}{-}CH(Cl)Re(CO)_5$. This is possibly caused by an additional interaction of the chlorine with the adjacent $Re(CO)_5$-group. The *cis/trans* mixture may arise through free rotation around the C(1)–C(2) bond of the anion, followed by the elimination of the Cl^- anion.

The interaction of 2-chlorovinyl ketones with the $[Mn(CO)_5]^-$ and $[C_5H_5Mo(CO)_3]^-$ anions is more complicated, however, and does not lead to any of the usual products expected from acylvinylation.

The solid *trans*-2-acylvinyl derivatives of iron or rhenium are quite stable in air, but the derivatives of tungsten gradually decompose even in the absence of light. Crystals of *cis*-$RCOCH{=}CHRe(CO)_5$, (IV), readily lose CO, however, and yield the complexes (V) spontaneously even in the dark. The NMR spectra show that this reaction is even more pronounced in the presence of a solvent, *e.g.*, (IVa) when dissolved in heptane produces a mixture of equal amounts of (IVa) and (Va) at room temperature after $1\frac{1}{2}$ h. After 24 h, (IVa) is quantitatively converted to (Va). This easy transformation provides important evidence in favour of the *cis*-structure of these compounds. Traces of HCl cause rapid *cis*→*trans* isomerisation of $RCOCH{=}CHRe(CO)_5$.

The structures of the σ-complexes thus obtained have been verified through IR and NMR spectra, (see Table 1). The IR spectra of compounds (Va, b) do not contain any bands corresponding to a free keto group. On the other hand, they contain a band at about 1460 cm^{-1} which may be assigned to a C=O group coordinated at a metal. In the analogous complexes of manganese, the bands presumably responsible for the coordinated keto group lie at 1500 to 1570 cm^{-1}, (ref. 7, 8).

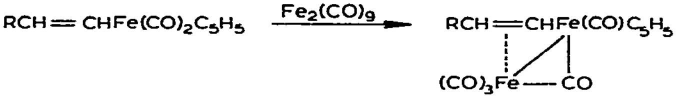
σ-Vinyl derivatives of iron, with no keto group adjacent to the double bond, have been synthesized through photodecarbonylation of the respective σ-acyl compounds. This reaction yields σ-vinyl-π-cyclopentadienyliron dicarbonyl[9] and a novel compound, *trans*-σ-styryl-π-cyclopentadienyliron dicarbonyl.

$$RCH{=}CHCOCl + NaFe(CO)_2C_5H_5 \rightarrow \underset{(VIa,\ b)}{RCH{=}CHCOFe(CO)_2C_5H_5} \xrightarrow[-CO]{h\nu}$$

$$\underset{(VIIa,\ b)}{RCH{=}CHFe(CO)_2C_5H_5}$$

a, R = H; b, R = C_6H_5

The σ-derivatives of iron, tungsten, and rhenium (I), (II), (III), and (VII) thus obtained have been further reacted with $Fe_2(CO)_9$ to give the binuclear complexes. Iron σ-vinyls, when heated with iron nonacarbonyl in benzene at 40°, produce the binuclear compound, (VIII), containing a Fe–Fe bond and a bridging CO group[10].

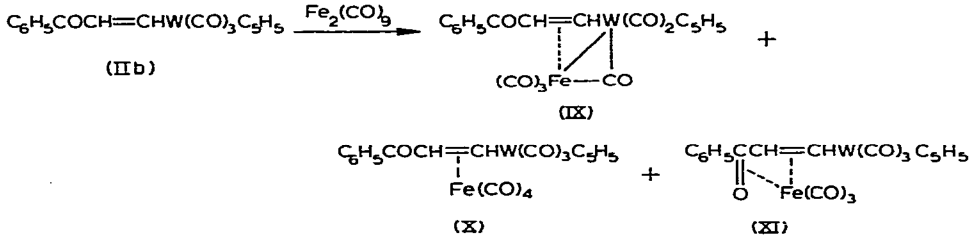


(VIII a-d)

(Ia), R= *trans*-CH_3CO
(Ib), R= *trans*-C_6H_5CO
(VIIa), R = H
(VIIb), R= *trans*-C_6H_5

(VIIIa) R=*trans*-CH_3CO
(VIIIb) R=*trans*-C_6H_5CO
(VIIIc) R=H
(VIIId) R=*trans*-C_6H_5

Under similar conditions, a σ-derivative of tungsten, $C_6H_5COCH{=}CHW(CO)_3C_5H_5$, yields binuclear complexes of different types: the complex (IX) containing an intermetallic bond, similar to the Fe–Fe complexes (VIII), and the compounds (X) and (XI) in which such a bond is absent[3].



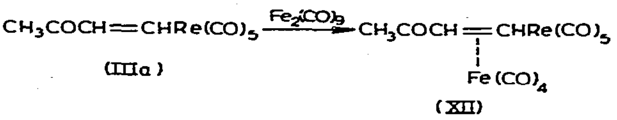
(IIb)

(IX)

(X)

(XI)

trans-$CH_3COCH{=}CHRe(CO)_5$ on the other hand, reacts with $Fe_2(CO)_9$ yielding only a binuclear complex in which a direct metal–metal bond is absent. It follows, therefore, that the structures of the binuclear complexes formed from iron nonacarbonyl and the transition metal σ-vinyls are very dependent on the nature of the metal.

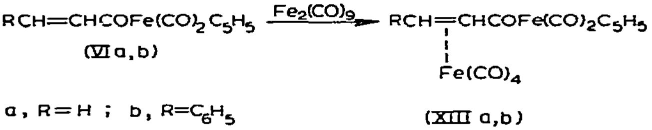


$$CH_3COCH{=}CHRe(CO)_5 \xrightarrow{Fe_2(CO)_9} CH_3COCH{=}CHRe(CO)_5 \cdot Fe(CO)_4$$

(IIIa) (XII)

It has been shown that iron nonacarbonyl forms σ,π-binuclear complexes not only with σ-2-acylvinyl derivatives of iron in which the olefinic group is adjacent to acyl, but also with the unsubstituted σ-vinyl and σ-styryl derivatives. Presumably, Fe–Fe bond formation stabilises the complexes (VIIc, d) in comparison with the π-ethylenic complexes of iron carbonyls[11]. Thus, the synthesis of σ,π-binuclear complex having an intermetallic bond does not require the presence of an electron-withdrawing group (e.g., acyl).

The formation of complexes containing a metal–metal bond does however depend on the presence of a double bond adjacent to the metal in the initial σ-derivative. If only one carbon atom is inserted in between the metal atom and the double bond, as in the σ-acyls $RCH{=}CHCOFe(CO)_2C_5H_5$ (VI), then reaction with $Fe_2(CO)_9$ in benzene at 40° will result in the formation of π-iron tetracarbonyl binuclear complexes (XIII). These compounds are formed in a good yield and contain

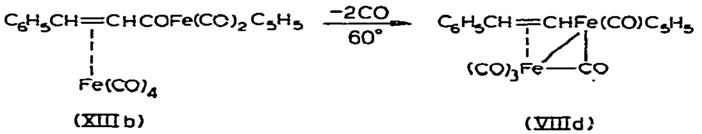


$$RCH{=}CHCOFe(CO)_2C_5H_5 \xrightarrow{Fe_2(CO)_9} RCH{=}CHCOFe(CO)_2C_5H_5 \cdot Fe(CO)_4$$

(VIa,b) (XIII a,b)

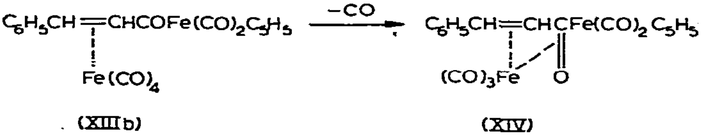
a, R=H ; b, R=C_6H_5

no metal–metal bonds. At 60° in benzene, complex (XIIIb) loses two molecules of carbon monoxide and yields the σ,π-binuclear complex (VIIId) containing a Fe–Fe bond as described above. Starting from this reaction the simple one-step synthesis of



(XIIIb) (VIIId)

the σ,π-binuclear complex (VIIId) may be achieved by heating σ-cinnamoyl-π-cyclopentadienyliron dicarbonyl (VIb) with iron nonacarbonyl in benzene at 40° for seven hours. Transformation of (XIIIb) to (VIId) cannot, however, be achieved photolytically, for UV irradiation of (XIIIb) leads to a π-iron tricarbonyl complex, (XIV), similar to the complexes of α,β-unsaturated ketones observed earlier[12,13].



(XIIIb) (XIV)

The σ-allyl derivative, $CH_2{=}CHCH_2Fe(CO)_2C_5H_5$, also fails to give the binuclear complex in its reaction with either $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$.

In addition the interaction of σ-(2-acylvinyl)-π-cyclopentadienyliron dicarbonyls (I) with $M(CO)_6$, $(CH_3CN)_3M(CO)_3$, and $(CH_3CN)M(CO)_5$, where M is Mo, W has also been studied. Irrespective of the reaction conditions, only the initial reactants or their decomposition products were isolated. Thus, $Fe_2(CO)_9$ could not be replaced by a Group VI metal carbonyl, or by its derivatives, in any of the reactions studied.

The structures of the binuclear complexes obtained have also been verified through the use of IR and NMR spectra (Table 1). In addition that of complex (VIIIa) has been verified by X-ray analysis[14,15]. The IR spectra of all the binuclear complexes, irrespective of the presence or absence of an intermetallic bond, are characterised by a 130 to 140 cm^{-1} decrease in the C=C double bond frequency, which may be assigned to coordination at an iron carbonyl group[2,12,13]. The iron tricarbonyl complex (XIV), whose keto group is coordinated, displays two intense bands at 1467 and 1425 cm^{-1} instead of the bands expected for a free C=O and a free C=C. This is similar to the change in the ligand IR spectra exhibited by α,β-unsaturated ketones coordinated to an iron carbonyl group[12,13]. Binuclear complexes with a metal–metal bond, in contrast to those in which such a bond is absent, exhibit IR bands corresponding to bridging carbonyls.

The ^1H NMR spectra of Fe–Fe bond binuclear complexes are characterised by a pronounced shift of the olefinic signals in comparison to those exhibited by the initial σ-vinyl compounds. The low-field signal (at about 11 ppm) has been assigned to the proton nearest to the σ-bonded iron. This assignment is based on the similarity of the signal to the respective signal in the spectrum of the σ,π-diiron complex (VIIIc). The spectrum of the latter contains three quartets of olefinic protons (a typical AMX system) which can be assigned unambiguously. Chemical shifts of olefinic protons differ by ca. 8 ppm for complexes (VIII) while the difference is below 4 ppm for the W–Fe analogue[4] (IX).

EXPERIMENTAL

General

IR spectra were recorded using KBr pellets or cyclohexane solutions on UR-20 and IKS-14A machines. NMR spectra were recorded on Perkin–Elmer R-12 and Hitachi–Perkin–Elmer R-20 spectrometers. Unless otherwise stated, the solvent was $CDCl_3$. The concentrations were 5 to 10%, hexamethyldisiloxane was used as an internal standard. All compounds were synthesized and isolated in an inert gas (nitrogen, argon) atmosphere, absolute solvents being used throughout.

(1). σ-Vinyl derivatives

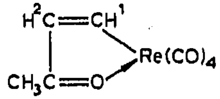
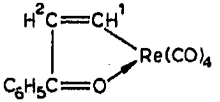
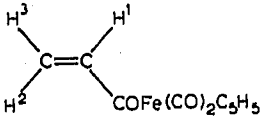
σ-2-Acylvinyl derivatives of Fe, W, and Re were synthesized from the respective Na-derivatives of metal carbonyls and a small excess of the 2-chlorovinyl ketone in THF. Details of the syntheses of Fe and W derivatives are given elsewhere[3,4].

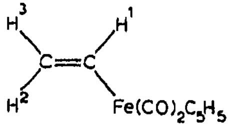
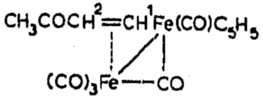
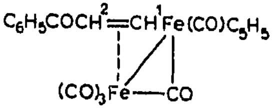
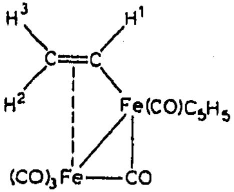
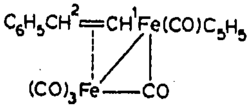
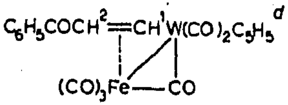
Interaction between $NaRe(CO)_5$ and $CH_3COCH{=}CHCl$. A solution of $NaRe(CO)_5$[16] (6.2 mmole) in 50 ml THF was added to a stirred solution of $CH_3COCH{=}CHCl$ (0.7 g, 6.7 mmole) in 30 ml THF at −78° over a period of 10 min. The mixture was stirred for an h at −78°, heated to room temperature over a period of 2 h, and stirred for a further h. The filtrate was evaporated *in vacuo*, and the residue separated on alumina (TLC, hexane/chloroform, 3/1) to give (a) traces of $Re_2(CO)_{10}$ and (Va),

(continued on p. 265)

TABLE 1

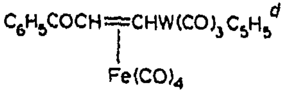
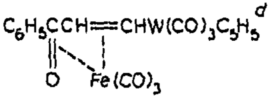
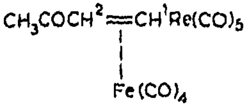
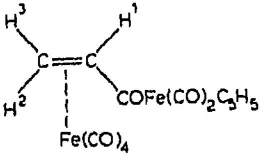
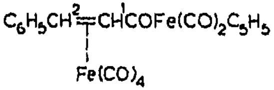
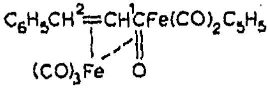
IR AND PMR SPECTRA OF THE COMPOUNDS STUDIED

Compound		$\nu(cm^{-1})$				δ(ppm)				$J(H^1-H^2)$ (Hz)
		C≡O[a]		C=O[b]	C=C[b]	H^1	H^2	C_5H_5	R	
(Ia)	$CH_3COCH^2{=}CH^1Fe(CO)_2C_5H_5$[c]	1980	2030	1641	1534	8.77	6.36	4.86	1.98	16.4
(Ib)	$C_6H_5COCH^2{=}CH^1Fe(CO)_2C_5H_5$[c]	1980	2030	1638	1512	9.21	7.16	4.87	7.75 *o* 7.32 *m,p*	16.3
(IIa)	$CH_3COCH{=}CHW(CO)_3C_5H_5$[d]	1947	2030	1651	1540					
(IIb)	$C_6H_5COCH^2{=}CH^1W(CO)_3C_5H_5$[d]	1947	2030	1644	1523	9.53	7.53	5.63	7.88 *o* 7.41 *m,p*	16.0
(IIc)	*p*-$BrC_6H_4COCH^2{=}CH^1W(CO)_3C_5H_5$[d]	1947	2030	1653	1524	9.58	7.47	5.75	7.83 *o* 7.67 *m*	16.2
(IIIa)	*trans*-$CH_3COCH^2{=}CH^1Re(CO)_5$	2004 s 2030 s	2141 w	1665	1548	8.65	6.92		2.19	18.7
(IIIb)	*trans*-$C_6H_5COCH^2{=}CH^1Re(CO)_5$	1955 s 2023 s	2133 w	1655	1545	8.98	7.67		7.87 *o* 7.42 *m,p*	18.1
(IVa)	*cis*-$CH_3COCH^2{=}CH^1Re(CO)_5$[e]	2004 s 2030 s	2141 w	1665	1550	8.21	7.62		2.19	13.0
(IVb)	*cis*-$C_6H_5COCH^2{=}CH^1Re(CO)_5$[e]	1995 s 2022 s 2032 s	2077 s 2141 m	1650	1540	8.58	8.34		7.97 *o* 7.51 *m,p*	13.0
(Va)		1950 s 2000 s	2102 m	1455	1570	10.86 10.63[e]	7.69 7.55[e]		2.50 2.46[e]	10.5 10.2[e]
(Vb)		1950 s 2001 s	2100 m	1465	1540	10.90	8.26		8.05 *o* 7.51 *m,p*	10.2
(VIa)		1966	2025	1610	1586	6.59	5.33	4.87	4.89(H^3)[f]	17.0

(VIb)	$C_6H_5CH^2{=}CH^1COFe(CO)_2C_5H_5$	1964 2015	2025	1622	1581	6.96	6.68	4.87	7.18–7.68	16.0
(VIIa)		1971	2022		1560	7.14	5.42	4.81	5.90(H³)[g]	17.4
(VIIb)	$C_6H_5CH^2{=}CH^1Fe(CO)_2C_5H_5$	1979	2029		1556	7.66	6.63	4.83	7.08–7.48	16.0
(VIIIa)		1803 1980 1994	2004 2054	1673	1400	11.34	2.20	5.05	1.93	10.0
(VIIIb)		1804 1980 1994	2006 2058	1640	1396	11.60	2.96	5.09	About 7.3	10.0
(VIIIc)		1818 1970 1985	1988 2023 2047		1420	10.91	1.70	5.00	2.22(H³)[h]	11.8
(VIIId)		1809 1970 1984	1988 2022 2042		1420	11.00	3.28	5.08	7.08–7.34	12.0
(IX)		1881 s 1937 s 2000 s	2009 s 2018 w 2079 s	1631	1400	8.14	4.19	5.39	7.98 *o* 7.44 *m,p*	10.0

(*continued*)

TABLE 1 *(continued)*

Compound		ν(cm^{-1})				δ(ppm)				$J(H^1-H^2)$ (Hz)
		C≡O[a]		C=O[b]	C=C[b]	H^1	H^2	C_5H_5	R	
(X)	 $C_6H_5COCH{=}CHW(CO)_3C_5H_5$[d] with $Fe(CO)_4$	1943 s 1954 s 1968 m 1988 m	2008 s 2031 s 2067 s	1633	1430					
(XI)	 $C_6H_5CCH{=}CHW(CO)_3C_5H_5$[d] with O and $Fe(CO)_3$	1937 w 1950 m 1956 m 1981 m	1992 s 2008 s 2059 s	1478 1450						
(XII)	 $CH_3COCH^2{=}CH^1Re(CO)_5$ with $Fe(CO)_4$	1968 s 1988 m 2000 m 2012 s	2020 s 2065 s 2108 w	1690	1410	8.85	4.69		2.21	13.3
(XIIIa)		1960 1988 2020 2027	2033 2093 2096	1600 1620	1420	3.94	2.57	4.90	2.19(H^3)[f]	11.5
(XIIIb)	 $C_6H_5CH^2{=}CH^1COFe(CO)_2C_5H_5$ with $Fe(CO)_4$	1960 1989 2017	2023 2031 2090	1600	1420	4.74	4.74	5.00	7.14–7.70	
(XIV)	 $C_6H_5CH^2{=}CH^1CFe(CO)_2C_5H_5$ with O and $(CO)_3Fe$	1970 1978 1984 1989	2026 2051 2057	1425 1467		5.55	3.42	5.07	7.31	9.3

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[a] In C_6H_{12}. [b] In KBr pellets. [c] See ref. 3, 10. [d] See ref. 4. [e] NMR spectrum recorded in CH_2Cl_2. [f] $J(H^1-H^3)$ 10.0; $J(H^2-H^3)$ 1.5 Hz. [g] $J(H^1-H^3)$ 9.0; $J(H^2-H^3)$ 1.4 Hz. [h] $J(H^1-H^3)$ 7.3; $J(H^2-H^3)$ 1.4 Hz. [i] $J(H^1-H^3)$ 7.0; $J(H^2-H^3)$ 1.7 Hz.

(b) 0.36 g (15%) pale-yellow crystals of *cis*-$CH_3COCH{=}CHRe(CO)_5$ (IVa), m.p. 59–60° (pentane), and (c) 0.48 g (20%) colourless crystals of *trans*-$CH_3COCH{=}CHRe(CO)_5$ (IIIa) m.p. 88–89° (methanol). [Found: (IVa): C, 27.29; H, 1.31; Re, 47.04. (IIIa): C, 27.53; H, 1.48; Re, 46.45. $C_9H_5O_6Re$ calcd.: C, 27.34; H, 1.28; Re, 47.10%.]

Interaction between $NaRe(CO)_5$ and $C_6H_5COCH{=}CHCl$. Similarly, $NaRe(CO)_5$ (6.2 mmole) was reacted with $C_6H_5COCH{=}CHCl$ (1.2 g, 7.2 mmole) dissolved in 30 ml THF. TLC separation gave (*a*) traces of $Re_2(CO)_{10}$, 0.21 g (8%) (Vb), bright-yellow crystals, m.p. 66° (pentane). (Found: C, 36.24; H, 1.71; Re, 43.14. $C_{13}H_7O_5Re$ calcd.: C, 36.36; H, 1.64; Re, 43.36%.) Also obtained were (*b*) 0.22 g (8%) of pale-yellow *cis*-$C_6H_5COCH{=}CHRe(CO)_5$ (IVb), m.p. 70° (pentane), and (*c*) 0.76 g (27%) of colourless *trans*-$C_6H_5COCH{=}CHRe(CO)_5$ (IIIb), m.p. 116–117° (methanol). [Found: (IVb): C, 36.76; H, 1.57; Re, 40.67. (IIIb): C, 36.78; H, 1.70; Re, 40.65. $C_{14}H_7O_6Re$ calcd.: C, 36.76; H, 1.54; Re, 40.71%.]

Synthesis of (Va). A solution of 0.1 g (IVa) in 20 ml hexane was heated at 30° for 3 h. The solvent was removed *in vacuo*. The products were separated on alumina (TLC) to give traces of (IIIa) and (IVa), and 0.06 g (65%) of yellow (Va), m.p. 40–41° (pentane). (Found: C, 26.23; H, 1.43; Re, 50.11. $C_8H_5O_5Re$ calcd.: C, 26.16; H, 1.37; Re, 50.69%.)

UV irradiation of $C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$ (VIb). A solution of 1.5 g (VIb) in 150 ml THF was irradiated for 9 h, filtered, and the solvent was removed *in vacuo*. The residue was chromatographed on alumina to give three fractions. The first (pale-yellow), after purification using TLC, gave 0.21 g (15%) of $C_6H_5CH{=}CHFe(CO)_2C_5H_5$ (VIIb). The second fraction (brown) gave 0.3 g (~35%) of $[C_5H_5Fe(CO)_2]_2$. The third fraction (yellow) contained 0.38 g (~25%) of initial (IVb). The compound (VIIb) melted at 46–47° (dec.; pentane). (Found: C, 64.42; H, 4.38; Fe, 19.77. $C_{15}H_{12}O_2Fe$ calcd.: C, 64.32; H, 4.32; Fe, 19.94%.)

(2). *Binuclear complexes*

These were generally obtained by heating the σ-derivatives of Fe, W, or Re with $Fe_2(CO)_9$ in benzene at 40° for 2 h. The interaction of the σ-2-acylvinyl compounds of Fe and W with $Fe_2(CO)_9$ is described in detail elsewhere[4,10].

Interaction between trans-$CH_3COCH{=}CHRe(CO)_5$ (IIIa) and $Fe_2(CO)_9$. The products obtained from the standard reaction of 1 g $CH_3COCH{=}CHRe(CO)_5$ (IIIa) and 1 g $Fe_2(CO)_9$ were separated on alumina by TLC. In this way 0.17 g (17%) of the initial reactant (IIIa) and 0.15 g (10%) of the complex $[CH_3COCH{=}CHRe(CO)_5]Fe(CO)_4$, m.p. 80° (dec.; pentane) were obtained. (Found: C, 27.40; H, 0.92; Fe, 10.06. $C_{13}H_5O_{10}FeRe$ calcd.: C, 27.72; H, 0.89; Fe, 9.92%.)

Interaction between $CH_2{=}CHFe(CO)_2C_5H_5$ (VIIa) and $Fe_2(CO)_9$. Similarly, 0.45 g $CH_2{=}CHFe(CO)_2C_5H_5$ and 0.8 g $Fe_2(CO)_9$ gave 75 mg (10%) (VIIIc). After crystallisation from pentane, the green compound decomposed at 100 to 120°C without melting. (Found: C, 41.67; H, 2.58; Fe, 31.50. $C_{12}H_8O_5Fe_2$ calcd.: C, 41.91; H, 2.34; Fe, 32.48%.) In addition, insignificant amounts of ferrocene and $[C_5H_5Fe(CO)_2]_2$ were found.

Interaction between $C_6H_5CH{=}CHFe(CO)_2C_5H_5$ (VIIb) and $Fe_2(CO)_9$. The standard reaction of 0.2 g (VIIb) and 0.3 g $Fe_2(CO)_9$ gave 63 mg (~20%) of the binuclear complex (VIIId). After crystallisation from methanol, the dark-green compound decomposed at 100 to 120° without melting. (Found: C, 51.50; H, 2.82; Fe, 26.69. $C_{18}H_{12}O_5Fe_2$ calcd.: C, 51.47; H, 2.88; Fe, 26.60%.)

Interaction between $C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$ *(VIb) and* $Fe_2(CO)_9$. In a similar manner, 2 g (VIb) and 2.4 g $Fe_2(CO)_9$ gave 1.6 g (50%) of $[C_6H_5CH{=}CHCOFe(CO)_2C_5H_5]Fe(CO)_4$ (XIIIb), yellow crystals, m.p. 101–102° (dec.; hexane). (Found: C, 50.52; H, 2.60; Fe, 23.23. $C_{20}H_{12}O_7Fe_2$ calcd.: C, 50.46; H, 2.54; Fe, 23.47%.)

Thermal reaction of $[C_6H_5CH{=}CHCOFe(CO)_2C_5H_5]Fe(CO)_4$ *(XIIIb)*. A solution of 0.6 g (XIIIb) in 100 ml benzene was heated for 7 h at 60°, filtered, and the solvent removed *in vacuo*. The TLC separation of the residue gave 120 mg (~40%) of the σ-cinnamoyl derivative (VIb) and 52 mg (10%) of a binuclear complex with an intermetallic bond (VIIId), together with traces of $C_6H_5CH{=}CHFe(CO)_2C_5H_5$, $[C_6H_5CH{=}CHCOFe(CO)_2C_5H_5]Fe(CO)_3$ (XIV), and of $[C_5H_5Fe(CO)_2]_2$.

One-step synthesis of the complex (VIIId). A solution of 2 g $C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$ (VIb) in 40 ml benzene was stirred with 2.4 g $Fe_2(CO)_9$ at 60° for 7 h. The mixture was filtered, the solvent removed *in vacuo*, and the residue separated by TLC on alumina to give 0.22 g (8%) of the complex (VIIId) together with insignificant amounts of the initial (VIb) and traces of $C_6H_5CH{=}CHFe(CO)_2C_5H_5$, $[C_5H_5Fe(CO)_2]_2$, (XIIIb), and of (XIV).

UV irradiation of $[C_6H_5CH{=}CHCOFe(CO)_2C_5H_5]Fe(CO)_4$ *(XIIIb)*. The iron tetracarbonyl complex (XIIIb) (0.5 g) dissolved in 100 ml THF was irradiated for 5 h, filtered, and the solvent removed *in vacuo*. The residue separated by TLC on alumina gave (*a*) traces of $C_6H_5CH{=}CHFe(CO)_2C_5H_5$, the binuclear complex (VIIId), and of $[C_5H_5Fe(CO)_2]_2$, (*b*) 65 mg (20%) of $C_6H_5CH{=}CHCOFe(CO)_2C_5H_5$ (VIb) and (*c*) 106 mg (~20%) of the iron tricarbonyl complex $[C_6H_5CH{=}CHCOFe(CO)_2C_5H_5]Fe(CO)_3$ (XIV). After crystallisation from methanol, the complex (XIV) was found to be an orange crystalline compound, m.p. 105–110° (dec.). (Found: C, 50.87; H, 2.73; Fe, 24.39. $C_{19}H_{12}O_6Fe_2$ calcd.: C, 50.94; H, 2.70; Fe, 24.93%.)

Interaction between $CH_2{=}CHCOFe(CO)_2C_5H_5$ *(VIa) and* $Fe_2(CO)_9$. The standard reaction of 0.6 g $CH_2{=}CHCOFe(CO)_2C_5H_5$ and 1.5 g $Fe_2(CO)_9$ gave 0.55 g (35%) of $[CH_2{=}CHCOFe(CO)_2C_5H_5]Fe(CO)_4$ (XIIIa). Crystallisation from pentane gave a yellow compound, m.p. 43–55° (dec.). (Found: C, 42.21; H, 2.04; Fe, 27.91. $C_{14}H_8O_7Fe_2$ calcd.: C, 42.04; H, 2.02; Fe, 27.93%.)

Thermal reaction of $[CH_2{=}CHCOFe(CO)_2C_5H_5]Fe(CO)_4$ *(XIIIa)*. Compound (XIIIa), 0.15 g, was heated in 40 ml benzene for 6 h. Preparative TLC on alumina gave 60 mg (40%) of the initial (XIIIa). Traces of $CH_2{=}CHFe(CO)_2C_5H_5$, $[C_5H_5Fe(CO)_2]_2$, and of (VIIIc) were found.

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