Reaction Studies on Heterodinuclear Alkanediyl Complexes: Some Examples of Metalloselectivity

Holger B. Friedrich and John R. Moss *
Department of Chemistry, University of Cape Town, Rondebosch 7700, South Africa

---

The reactions of some heterobimetallic alkanediyl complexes of the type $[(\eta\text{-}C_5R_5)(OC)_2Fe(C_nH_{2n})ML_y]$ [R = H, n = 3–6, ML_y = $Mo(CO)_3(cp)$, $W(CO)_3(cp)$, $Ru(CO)_2(cp)$ or $Re(CO)_5$; R = Me, n = 3, ML_y = $Ru(CO)_2(cp)$; cp = $\eta\text{-}C_5H_5$] with tertiary phosphines, trityl hexafluorophosphate (Ph_3CPF_6) and halogens were investigated. The reactions of $[(cp)(CO)_2Fe(C_3H_6)ML_y]$ with PPh_3 were metalloselective, with the phosphine always attacking the expected metal site, which could be predicted from the reactivities of the corresponding monometallic alkyl or homodinuclear alkanediyl species. The alkanediyl chain length was found not to influence the site of nucleophilic attack. The reactions of $[(cp)(OC)_2Fe(C_3H_6)ML_y]$ [ML_y = $Ru(CO)_2(cp)$, $Mo(CO)_3(cp)$ or $W(CO)_3(cp)$] with Ph_3CPF_6 gave the complexes $[(cp)(OC)_2Fe(C_3H_5)ML_y]PF_6$, where the β-CH unit is believed to be weakly bonded to both metal centres. The reaction of $[(cp)(OC)_2Fe(C_nH_{2n})Ru(CO)_2(cp)]$ (n = 4 or 6) with the trityl salt was not metalloselective, and gave a mixture of equal amounts of $[(cp)(OC)_2Fe\{CH_2CH(CH_2)_{n-2}\}Ru(CO)_2(cp)]PF_6$ and $[(cp)(OC)_2Fe\{(CH_2)_{n-2}CHCH_2\}Ru(CO)_2(cp)]PF_6$. In contrast, $[(cp)(OC)_2Fe(C_4H_8)W(CO)_3(cp)]$ gave only $[(cp)(OC)_2Fe\{CH_2CH(CH_2)_2\}W(CO)_3(cp)]PF_6$. Metalloselectivity was observed for the reaction of $[(cp)(OC)_2Fe(C_6H_{12})W(CO)_3(cp)]$ with HCl, which gave cleavage of the W–C bond. In contrast, the reaction of $[(cp)(OC)_2Fe(C_5H_{10})Ru(CO)_2(cp)]$ with I_2 resulted in cleavage of both metal–alkyl bonds. The reactions of $[(cp)(OC)_3Mo(C_4H_8)Mo(CO)_3(cp)]$ with PPh_3 to give $[(cp)(OC)_2(Ph_3P)Mo\{C(O)(CH_2)_4\}Mo(CO)_3(cp)]$ and $[(cp)(OC)_2(Ph_3P)Mo\{C(O)(CH_2)_4C(O)\}Mo(PPh_3)(CO)_2(cp)]$ are also reported.

In contrast to homobimetallic alkanediyl complexes, few heterobimetallic alkanediyl complexes are known and few reactivity studies have been carried out on them.[1,2] The μ-methylene complex $[ClMe_2(bipy)PtCH_2Au(PPh_3)]$ (bipy = 2,2′-bipyridine) was reported to react with the electrophiles HCl, Cl_2 and $HgCl_2$ by selective cleavage of the Au–C bond to give $[Au(PPh_3)Cl]$ and $[Pt(CH_2Y)ClMe_2(bipy)]$, Y = H, Cl or HgCl respectively.[3] The reactions of the μ-ethylene complexes $[(OC)_5Re(C_2H_4)ML_y]$ [ML_y = $Mn(CO)_5$, $W(CO)_3(cp)$ or $Mo(CO)_3(cp)$; cp = $\eta\text{-}C_5H_5$] with $[Re(CO)_5]^-$ resulted in elimination of the ML_y group to form $[(OC)_5Re(C_2H_4)Re(CO)_5]$.[4–7] Thermolysis of the above heterobimetallic ethylene-bridged complexes gives ethylene and the metal–metal bonded dimers $[(ML_y)_2]$ as well as $[Re_2(CO)_{10}]$.[4,5,7] The reaction of $[(cp)_2ClZr(C_2H_4)AlEt_2]$ with $AlEt_3$ to give $[(cp)_2ClZrCH_2CH(AlEt_2)_2]$ has also been reported.[8] However, the only experiments carried out on a heterobimetallic alkanediyl complex where $n > 2$ appear to be a study of the thermal decomposition of $[(cp)(OC)_2Fe(C_3H_6)Ru(CO)_2(cp)]$.[9]

The study of heterodinuclear metal alkyl complexes is particularly interesting since, with different metals present within the same molecule, there exists the possibility of metalloselective reactions and of one metal influencing the reactivity of the other. We have recently reported the preparation of a range of heterobimetallic complexes[10,11] and now report on some of their reactions.

Results and Discussion

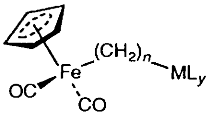
Reactions with Neutral Nucleophiles.—The heterobimetallic iron–molybdenum complex $[(cp)(OC)_2Fe(C_3H_6)Mo(CO)_3(cp)]$ **1** reacts with 1 mol PPh_3 in MeCN at room temperature to give a yellow precipitate which was identified as the monoacyl complex $[(cp)(OC)_2Fe\{(CH_2)_3C(O)\}Mo(PPh_3)(CO)_2(cp)]$ **2a**, equation (1). No evidence of reaction occurring at the iron side of the molecule was obtained. Similarly, PMe_2Ph reacts at the molybdenum side of complex **1** only, to give $[(cp)(OC)_2Fe\{(CH_2)_3C(O)\}Mo(PMe_2Ph)(CO)_2(cp)]$ **2b**. The length of the alkyl chain does not appear to affect the type of product obtained in the reactions of the iron–molybdenum alkanediyl complexes. Thus $[(cp)(OC)_2Fe(C_6H_{12})Mo(CO)_3(cp)]$ **3** reacts with PPh_3 to give the complex $[(cp)(OC)_2Fe\{(CH_2)_6C(O)\}Mo(PPh_3)(CO)_2(cp)]$ **4** only, as shown in equation (1). The reactions of $[(cp)(OC)_2Fe(C_4H_8)Mo(CO)_3(cp)]$ with L = PPh_3 or PMe_2Ph in tetrahydrofuran (thf) also resulted in nucleophilic attack only at the Mo to afford $[(cp)(OC)_2Fe\{(CH_2)_4C(O)\}MoL(CO)_2(cp)]$ as the only isolable products, albeit in low yields.

$$[(cp)(OC)_2Fe(C_nH_{2n})Mo(CO)_3(cp)] + L \longrightarrow [(cp)(OC)_2Fe\{(CH_2)_nC(O)\}MoL(CO)_2(cp)] \quad (1)$$

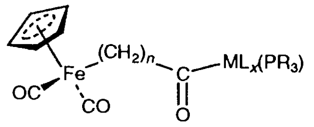
n = 3, L = PPh_3 **2a**, PMe_2Ph **2b** or CO **5**
n = 6, L = PPh_3 **4**

Complex **1** reacts with CO gas in MeCN at room temperature and atmospheric pressure. Infrared monitoring of the reaction solution showed the disappearance of a ν(CO)(Mo–CO) band at 2010 cm^{-1}, the concurrent growth of a band at 1943 cm^{-1} [also assignable to ν(CO)(Mo–CO)] and the appearance of an acyl band at 1645 cm^{-1}. This implied that the reaction occurred at Mo to form $[(cp)(OC)_2Fe\{(CH_2)_3C(O)\}Mo(CO)_3(cp)]$ **5**.

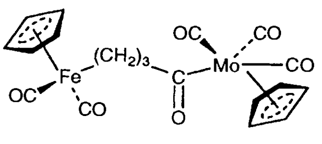
Thus, all these reactions of the iron–molybdenum alkanediyl complexes occurred at the molybdenum end of the molecule. This would be expected by comparison of the reactivities of the mononuclear alkyl complexes of iron and molybdenum, since molybdenum alkyl complexes undergo carbon monoxide insertion/alkyl migration reactions much more readily than their iron analogues.[12–14] The above results are also as expected from the reactivities of the homodinuclear alkanediyl complexes



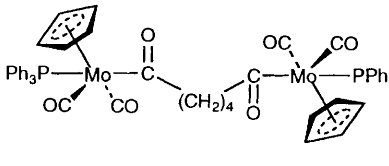
$n = 3$, $ML_y = Mo(CO)_3(cp)$ **1**, $Ru(CO)_2(cp)$ **7**, $W(CO)_3(cp)$ **9** or $Re(CO)_5$ **11**
$n = 6$, $ML_y = Mo(CO)_3(cp)$ **3**



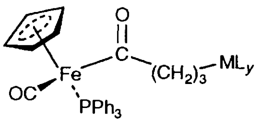
$n = 3$, $ML_x = Mo(CO)_2(cp)$, $PR_3 = PPh_3$ **2a** or PMe_2Ph **2b**
$n = 6$, $ML_x = Mo(CO)_2(cp)$, $PR_3 = PPh_3$ **4**



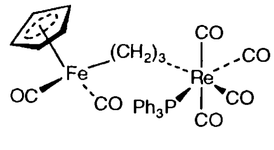
5



6



$ML_y = Ru(CO)_2(cp)$ **8**, $W(CO)_3(cp)$ **10** or $Re(PPh_3)(CO)_4$ **13**



12

of Fe and Mo, as represented in equations (2) and (3) [M = Fe,

$$[L_y(OC)M(C_nH_{2n})M(CO)L_y] + PR_3 \xrightarrow{k_1} [L_y(R_3P)M\{C(O)(CH_2)_n\}M(CO)L_y] \quad (2)$$

$$[L_y(R_3P)M\{C(O)(CH_2)_n\}M(CO)L_y] + PR_3 \xrightarrow{k_2} [L_y(R_3P)M\{C(O)(CH_2)_nC(O)\}M(PR_3)L_y] \quad (3)$$

L_y = (cp)(CO); M = Mo, L_y = (cp)(CO)$_2$]. For M = Fe $k_1 > k_2$, whilst for M = Mo, $k_1 \approx k_2$. Also, k_1 is greater for Mo than for Fe. Thus, the reaction of $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_3H_6)]$ with 1 equivalent of PPh_3 gives $[(cp)(OC)(Ph_3P)Fe\{C(O)(CH_2)_3\}Fe(CO)_2(cp)]$, whilst $[\{Mo(CO)_3(cp)\}_2(\mu\text{-}C_4H_8)]$ with 1 equivalent of PPh_3 gives a 10:7 mixture of $[(cp)(OC)_2(Ph_3P)Mo\{C(O)(CH_2)_4\}Mo(CO)_3(cp)]$ and $[(cp)(OC)_2(Ph_3P)Mo\{C(O)(CH_2)_4C(O)\}Mo(PPh_3)(CO)_2(cp)]$ **6**. The reaction of $[\{Mo(CO)_3(cp)\}_2(\mu\text{-}C_4H_8)]$ with 2 equivalents of PPh_3 gives the diacyl complex **6** only. Complex **6** is reported for the first time. The IR, ^1H and ^{13}C NMR data suggest that all the above phosphine-substituted molybdenum centres have a *trans* stereochemistry (Tables 1–3).

The reaction of $[(cp)(OC)_2Fe(C_3H_6)Ru(CO)_2(cp)]$ **7** with 1 equivalent of PPh_3 in refluxing thf gave exclusively $[(cp)(OC)(Ph_3P)Fe\{C(O)(CH_2)_3\}Ru(CO)_2(cp)]$ **8** in good yield. Thus the nucleophile, PPh_3, attacked complex **7** only at the iron side of the molecule. Again, this is as expected since iron–carbonyl alkyl complexes are known to undergo migratory insertion reactions with tertiary phosphines in thf,[13,14] whilst corresponding ruthenium complexes do so much more reluctantly.[15,16] The homometallic alkanediyl complexes of iron and ruthenium show similar reactivity patterns to those of their monometallic alkyl analogues.[17,18] Infrared monitoring of separate but concurrent reactions of equal quantities of $[(cp)(OC)_2Fe(C_3H_6)Ru(CO)_2(cp)]$ and $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_3H_6)]$ with 1 mol PPh_3 each in refluxing thf indicated that the former reaction was complete first. This suggested that the Fe atom was slightly activated towards phosphine attack by the presence of the Ru atom in the same molecule. These data are, however, qualitative and further measurements are necessary before a more detailed interpretation of these results is made.

As might have been anticipated from studies of $[W(CO)_3(cp)R]$[19,20] and $[Fe(CO)_2(cp)R]$[13,14] compounds, the reaction of $[(cp)(OC)_2Fe(C_3H_6)W(CO)_3(cp)]$ **9** with 1 equivalent of PPh_3 gave the complex $[(cp)(OC)(Ph_3P)Fe\{C(O)(CH_2)_3\}W(CO)_3(cp)]$ **10** as a yellow solid in 68% yield. No evidence for any substitution or migratory insertion reaction at W was observed. The reaction of $[(cp)(OC)_2Fe(C_3H_6)Re(CO)_5]$ **11** with 1 mol PPh_3 in refluxing thf (70 h) gave $[(cp)(OC)_2Fe(C_3H_6)Re(PPh_3)(CO)_4]$ **12** as an oily orange solid in *ca.* 60% yield [equation (4)]. A small quantity of $[(cp)(OC)(Ph_3P)Fe\{C(O)(CH_2)_3\}Re(PPh_3)(CO)_4]$ **13** was also obtained, probably from further reaction of complex **12** with PPh_3. Thus, the initial reaction of PPh_3 with complex **11** appears to be metalloselective, with PPh_3 preferentially attacking at the Re and resulting in carbonyl substitution. This selectivity is remarkable, since the rates of the reactions of the diiron and dirhenium alkanediyl complexes with PPh_3 in thf appear to be very similar.[18,21,22] Infrared evidence (Table 1) indicates that complexes **12** and **13** have a *cis* configuration at rhenium.

$$[(cp)(OC)_2Fe(C_3H_6)Re(CO)_5] + PPh_3 \longrightarrow [(cp)(OC)_2Fe(C_3H_6)Re(PPh_3)(CO)_4] + CO \quad (4)$$

Both $[\{Fe(CO)_2(\eta\text{-}C_5Me_5)\}_2(\mu\text{-}C_4H_8)]$[22] and $[\{Ru(CO)_2(cp)\}_2(\mu\text{-}C_5H_{10})]$ **14**[17] have been reported to react very slowly with tertiary phosphines in both MeCN and thf. Complex **14** was however reported to react readily with PPh_3 in refluxing xylene.[17] The complex $[(\eta\text{-}C_5Me_5)(OC)_2Fe(C_3H_6)Ru(CO)_2(cp)]$ was treated with 1 mol equivalent of PPh_3 in refluxing xylene. Infrared monitoring of the carbonyl region of the reaction mixture showed the reaction to be complete after 38 h. At this stage only bands at 1922vs and 1752w cm^{-1} were observed in the ν(CO) region. The ^1H and ^{13}C NMR spectra of the product showed a mixture of two compounds, both with peaks characteristic of a phosphine-substituted (cp)Ru(CO) group.[16,17] Since no peaks in the region characteristic of a C_5Me_5 group were observed in either the ^1H or ^{13}C NMR spectrum, it appeared that the $(C_5Me_5)Fe$ group had decomposed under the reaction conditions. All attempts to separate or purify the reaction products were unsuccessful.

The generally predictable metalloselectivity in the above reactions contrasts with observations made on heterobimetallic complexes with direct metal–metal bonds, where the site of nucleophilic attack is not always predictable.[23]

The ^1H NMR spectra of the dinuclear acyl complexes show the expected triplet for the CH_2 protons α to the acyl group in **2a**, **2b**, **4**, **6** (Table 2) and $[(cp)(OC)_2Fe\{(CH_2)_4C(O)\}MoL(CO)_2(cp)]$, L = PPh_3 or PMe_2Ph (Experimental section). For the compounds **8**, **10** and **13**, however, two multiplets are observed for the $C(O)CH_2$ protons. This is because these protons are now adjacent to the chiral centre $(cp)(OC)(Ph_3P)Fe$ and are hence non-equivalent.[24–26] It would also be expected that each of these compounds would be mixtures of two diastereoisomers.

Table 1 Analytical[a] and physical data for the complexes

Complex	Yield (%)	M.p./°C	ν(CO)[b]/cm^{-1}	Analysis (%) C	H
2a $[(cp)(OC)_2Fe\{(CH_2)_3C(O)\}Mo(PPh_3)(CO)_2(cp)]$	68	150–153	1999s, 1938vs, 1850vs, 1607m	59.20 (59.50)	3.50 (4.25)
4 $[(cp)(OC)_2Fe\{(CH_2)_6C(O)\}Mo(PPh_3)(CO)_2(cp)]$	60	Oily solid	1998vs, 1937vs, 1850vs, 1614m	60.10 (60.90)	4.70 (4.80)
6 $[(cp)(OC)_2(Ph_3P)Mo\{C(O)(CH_2)_4C(O)\}Mo(PPh_3)(CO)_2(cp)]$	73	161–165	1935s, 1853vs, 1611m	62.60 (62.75)	4.30 (4.50)
8 $[(cp)(OC)(Ph_3P)Fe\{C(O)(CH_2)_3\}Ru(CO)_2(cp)]$	45	149–150	2009vs, 1944vs, 1912s, 1603m	59.50 (59.70)	4.70 (4.40)
10 $[(cp)(OC)(Ph_3P)Fe\{C(O)(CH_2)_3\}W(CO)_3(cp)]$	68		2007s, 1911vs, 1603w	53.00 (53.05)	4.00 (3.80)
12 $[(cp)(OC)_2Fe(C_3H_6)Re(PPh_3)(CO)_4]$	63	Oily solid	2072m, 2010m, 1996s, 1965vs, 1933s	48.80 (49.30)	3.10 (3.35)
13 $[(cp)(OC)(Ph_3P)Fe\{C(O)(CH_2)_3\}Re(PPh_3)(CO)_4]$	7	65–71	2074m, 2033m, 1990m, 1964vs, 1922s, 1602m	57.70 (57.60)	4.00 (3.95)
16 $[(cp)(OC)_2Fe(C_3H_5)Mo(CO)_3(cp)]PF_6$	30	> 180 (decomp.)	2067s, 2021s,[c] 1944 (sh), 1909s	34.90 (35.55)	2.30 (2.45)
17 $[(cp)(OC)_2Fe(C_3H_5)Ru(CO)_2(cp)]PF_6$	74	182–187 (decomp.)	2076 (sh), 2030 (sh),[c] 2002s, 1948 (sh)	34.70 (34.85)	2.60 (2.60)
19 $[(cp)(OC)_2Fe(C_4H_7)Ru(CO)_2(cp)]PF_6$	51	102–119	2079s, 2037s, 2010s, 1950s	36.20 (36.05)	3.00 (2.85)
20 $[(cp)(OC)_2Fe(C_4H_7)W(CO)_3(cp)]PF_6$	55	149–153 (decomp.)	2075w, 2036w 2014w, 1922 (sh), 1912w	32.30 (32.15)	2.60 (2.40)
21 $[(cp)(OC)_2Fe(C_6H_{11})Ru(CO)_2(cp)]PF_6$	71		2082vs, 2039vs, 2009vs, 1943vs	38.20 (38.25)	3.30 (3.35)

[a] Required values in parentheses. [b] In CH_2Cl_2. [c] As Nujol mull.

Reactions with the Trityl Salt Ph_3CPF_6.—The complex $[(cp)(OC)_2Fe(C_3H_6)Fe(CO)_2(cp)]$ has been shown to react with Ph_3CPF_6 to give $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}CH_2CHCH_2)]PF_6$ **15**.[27] A crystal-structure analysis showed that complex **15** exists as a transition-metal-stabilised carbonium ion with the positive charge located on the central carbon atom of the three-carbon chain.[28] The iron atoms were shown to be weakly linked to the β-CH group of the allylic system (Fig. 1). The reactions of $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_nH_{2n})]$ (n = 4–6) with Ph_3CPF_6 gave yellow crystalline complexes of formula $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_nH_{2n-1})]PF_6$.[29] These complexes are believed to have structures in which one iron atom is π bonded and the other σ bonded to the alkyl chain (Fig. 2).

The complex $[(cp)(OC)_3Mo(C_4H_8)Mo(CO)_3(cp)]$ was also found to react with the trityl salt, although much more slowly than the analogous reaction of $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_4H_8)]$. The product, which may be $[\{Mo(CO)_3(cp)\}_2(\mu\text{-}C_4H_7)]PF_6$, was very unstable in solution and not isolated in pure form or completely characterised.

The reaction of $[(cp)(OC)_2Fe(C_3H_6)Mo(CO)_3(cp)]$ **1** with the trityl salt gave $[(cp)(OC)_2Fe(C_3H_5)Mo(CO)_3(cp)]PF_6$ **16** as lustrous golden crystals in 30% yield. Complex **16** was insoluble in diethyl ether, very sparingly soluble in CH_2Cl_2 and sparingly soluble in acetone. Two possible structures exist for it. First, both the Fe and Mo atoms may be weakly linked to the β-CH group as shown for complex **15** in Fig. 1. Alternatively, one of the metals may be π bonded and the other σ bonded to the allyl group, *i.e.* a structure similar to that shown for $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_4H_7)]PF_6$ in Fig. 2.

The ^1H NMR spectrum of complex **16** at room temperature is similar to that observed for **15** at room temperature. However, at −30 °C it showed differences and the data with assignments are in Table 2. Since the protons of (cp)Fe in **16** are more deshielded than those of cp in **15**, it would seem that a higher positive charge resides on the Fe atom in complex **16**.

The ^{13}C NMR spectrum of complex **16** shows the (cp)Mo peak at δ 95.0 (3 ppm downfield when compared to the corresponding peak of **1** [10]), and the (cp)Fe is at δ 88.9 [4 ppm downfield when compared to the corresponding peak of **1**, and 2 ppm downfield relative to the (cp)Fe peaks of **15**]. A peak at δ 40.1 can be assigned to $FeCH_2$ and the peak at δ 9.2 to $MoCH_2$. The $FeCH_2$ peak is significantly deshielded relative to the corresponding peak for complex **15**, *i.e.* by *ca.* 16 ppm, whilst the $MoCH_2$ peak is only deshielded by 3 ppm relative to **1**. All these data suggest that the structure of complex **16** may be some sort of hybrid of the two 'limiting' types shown in Figs. 1 and 2, with the π bond tending to form on the iron side of the molecule.

The reaction of complex **7** with the trityl salt gave a product identified as $[(cp)(OC)_2Fe(C_3H_5)Ru(CO)_2(cp)]PF_6$ **17**. This complex was obtained as an orange solid and was insoluble in ether or CH_2Cl_2, but moderately soluble in acetone. The ^1H NMR spectrum was similar to that of **15**.[30] The peak positions and their assignments are shown in Table 2. Variable-temperature ^1H NMR spectra were also recorded. The

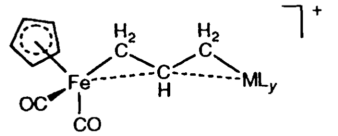
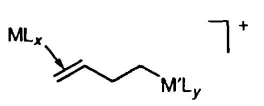


Fig. 1 Schematic diagram for complexes **15** [ML_y = $Fe(CO)_2(cp)$] and **17** [ML_y = $Ru(CO)_2(cp)$]



	ML_x	$M'L_y$
18	$Fe(CO)_2(cp)$	$Mo(CO)_3(cp)$
19a	$Fe(CO)_2(cp)$	$Ru(CO)_2(cp)$
19b	$Ru(CO)_2(cp)$	$Fe(CO)_2(cp)$
20	$Fe(CO)_2(cp)$	$W(CO)_3(cp)$
	$Fe(CO)_2(cp)$	$Fe(CO)_2(cp)$

Fig. 2 Proposed structure of complexes **18**–**20** and $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_4H_7)]PF_6$

Table 2 Proton NMR data[a] (δ) for the complexes

Complex	
2a	7.43 (s, 15 H, PPh_3), 4.99 [s, 5 H, Mo(cp)], 4.70 [s, 5 H, (cp)Fe], 3.08 [t, 2 H, $C(O)CH_2$, $^3J(PH) = 7.1$], 1.58 [qnt, 2 H, CH_2, $^3J(HH) = 5.6$], 1.31 (m, 2 H, $FeCH_2$)
2b	7.59, 7.40 (m, 5 H, Ph), 4.92 [d, 5 H, Mo(cp), $^3J(PH) = 1.4$], [4.68 s, 5 H, (cp)Fe], 3.01 [t, 2 H, $C(O)CH_2$, $^3J(PH) = 7.3$], 1.86 [d, 6 H, Me, $^2J(PH) = 8.9$], 1.48 [qnt, 2 H, CH_2, $^3J(HH) = 8.6$], 1.25 (m, 2 H, $FeCH_2$)
4	7.36 (m, 15 H, PPh_3), 4.95 [s, 5 H, (cp)Mo], 4.66 [s, 5 H, (cp)Fe], 3.00 [t, 2 H, $C(O)CH_2$, $^3J(PH) = 11.7$], 1.38 (s), 1.26 (s) [10 H, $(CH_2)_5$]
6	7.39 (s, 30 H, PPh_3), 4.96 [d, 10 H, Mo(cp), $^3J(PH) = 1.1$], 2.97 [t, 4 H, $C(O)CH_2$, $^3J(PH) = 6.5$], 1.35 [qnt, 4 H, $(CH_2)_2$, $J(HH) = 3.5$]
8	7.38 (m, 15 H, PPh_3), 5.18 [s, 5 H, (cp)Ru], 4.41 [d, 5 H, (cp)Fe, $^3J(HH) = 1.1$], 2.84, 2.60 [m, 2 H, $C(O)CH_2$], 1.38 [m, 4 H, $(CH_2)_2$]
10	7.46 (m, 15 H, PPh_3), 5.33 [s, 5 H, W(cp)], 4.40 [s, 5 H, (cp)Fe], 2.85 (m), 2.70 (m) [2 H, $C(O)CH_2$], 1.26 (m, 2 H), 0.88 (m, 2 H)
12	7.39 (m, 15 H, PPh_3), 4.61 [s, 5 H, (cp)Fe], 1.72 (m, 2 H, $FeCH_2$), 1.2 (m, 2 H, CH_2), 0.58 (m, 2 H, $ReCH_2$)
13	7.44 (m, 30 H, PPh_3), 4.35 [d, 5 H, (cp)Fe, $^3J(PH) = 1.1$], 2.65, 2.33 [m, 2 H, $C(O)CH_2$], 1.28 (m, 2 H, CH_2), 0.62 (m, 2 H, $ReCH_2$)
16[b]	5.78 [s, 5 H, Mo(cp)], 5.72 [s, 5 H, Fe(cp)], 6.41 (m, 1 H, CH), 3.30 [d, 1 H, $J(HH) = 8.5$], 3.28 [d, 1 H, $J(HH) = 13.3$], 2.83 (m, 1 H), 1.91 (m, 1 H)
17[b,c]	5.92 [s, 5 H, Ru(cp)], 5.33 [s, 5 H, Ru(cp)], 6.75 (m, 1 H, CH), 3.29 (m, 2 H, $FeCH_2$), 2.70 [t, 1 H, $RuCH_2$, $J(HH) = 4.8$], 2.17 [dd, 1 H, $RuCH_2$, $J(HH) = 4.7$ and 13.9]
19a	5.84 [s, 5 H, Fe(cp)], 5.45 [s, 5 H, Ru(cp)], 5.35 (m, 1 H, =CH), 3.93 [d, 1 H, $=CH_2$, $J(HH) = 8.2$], 3.50 [d, 1 H, $=CH_2$, $J(HH) = 14.8$], 2.53 (m, 2 H, CH_2), 1.87 (m, 2 H, $RuCH_2$)
19b[d]	6.12 [s, 5 H, Ru(cp)], 4.97 [s, 5 H, Fe(cp)], 3.92 [d, 1 H, =CH, $J(HH) = 8.5$], 3.86 [d, 1 H, $=CH_2$, $J(HH) = 14.4$], 1.61 (m, 2 H, CH_2), 1.25 (m, 2 H, $FeCH_2$)
20	5.86 [s, 5 H, Fe(cp)], 5.69 [s, 5 H, W(cp)], 5.33 (m, 1 H, =CH), 3.99 [d, 1 H, =CH, $J(HH) = 8.2$], 3.53 [d, 1 H, $=CH_2$, $J(HH) = 14.7$], 2.70 [tt, 1 H, CH_2, $J(HH) = 3.7$ and 11.7], 1.87 (m, 1 H, CH_2)

[a] In $CDCl_3$ using $SiMe_4$ as reference standard (δ 0.00), J in Hz, dd = doublet of doublets, tt = triplet of triplets. [b] Recorded at −30 °C. [c] Assignments aided by COSY and HETCOR experiments. [d] The =CH peak was not observed.

Table 3 Carbon-13 NMR data[a] (δ) for the complexes

Complex	
2a	267.0 [d, MoC(O), $^2J(PC) = 10.9$], 238.6 [d, MoCO, $^2J(PC) = 24.1$], 217.6 (s, FeCO), 135.6 (d), 133.1 (d), 130.3 (s), 128.5 (d) (PPh_3), 96.5 [s, Mo(cp)], 85.3 [s, (cp)Fe], 70.3 [s, $C(O)\mathit{C}H_2$], 34.0 [s, $C(O)CH_2\mathit{C}H_2$], 3.7 (s, $FeCH_2$)
2b	268.0 [d, MoC(O), $^2J(PC) = 11.9$], 237.8 [d, MoCO, $^2J(PC) = 24.0$], 217.5 (s, FeCO), 138.7 (d), 135.9 (d), 129.4 (d), 128.6 (d) (PPh_3), 95.6 [s, Mo(cp)], 85.2 [s, Fe(cp)], 70.5 [s, $C(O)\mathit{C}H_2$], 34.0 [s, $C(O)CH_2\mathit{C}H_2$], 19.8 (d, PMe_2), 3.8 (s, $FeCH_2$)
6	267.6 [d, MoC(O), $^2J(PC) = 10.5$], 238.0 [d, MoCO, $^2J(PC) = 24.2$], 135.4 (d), 132.9 (d), 130.1 (d) (PPh_3), 96.4 [s, Mo(cp)], 65.3 [s, $C(O)\mathit{C}H_2$], 25.0 [s, $C(O)CH_2\mathit{C}H_2$]
8	276.9 [d, FeC(O), $^2J(PC) = 22.4$], 202.3 (s, RuCO), 221.0 [d, FeCO, $^2J(PC) = 31.3$], 136.6 (d), 133.3 (d), 129.6 (d), 128.2 (d) (PPh_3), 88.5 [s, Ru(cp)], 85.2 [s, Fe(cp)], 71.5 [d, $C(O)\mathit{C}H_2$, $^3J(PC) = 5.3$], 35.3 [s, $C(O)CH_2\mathit{C}H_2$], −3.1 (s, $RuCH_2$)
10	229.5 (s, WCO), 136.6 (d), 133.4 (d), 129.7 (d), 128.0 (d) (PPh_3), 91.4 [s, W(cp)], 85.2 [s, Fe(cp)], 72.2 [s, $C(O)\mathit{C}H_2$], 32.8 [s, $C(O)CH_2\mathit{C}H_2$], 9.8 (s, WCH_2)
12	217.9 (s, FeCO), 193.0 [d, ReCO, $^2J(PC) = 9.8$], 190.4 [d, ReCO, $^2J(PC) = 41.2$], 188.2 [d, ReCO, $^2J(PC) = 6.8$], 133.3 (d), 130.5 (s), 128.5 (d) (PPh_3), 85.1 [s, Fe(cp)], 48.6, [d, $ReCH_2$, $^2J(PC) = 2.8$], 29.7 (s, CH_2), 12.5 (s, $FeCH_2$)
15	127.3 (CH), 87.7 [Fe(cp)], 24.0 ($FeCH_2$)
16	120.0 (CH), 95.0 [Mo(cp)], 88.9 [Fe(cp)], 40.1 ($FeCH_2$), 9.2 ($MoCH_2$)
17	123.5 (CH), 90.8 [Ru(cp)], 87.4 [Fe(cp)], 27.4 ($FeCH_2$), 18.5 ($RuCH_2$)
19a	211.3, 209.1 (FeCO),[b] 202.9 (RuCO), 90.5 (=CH), 89.9 [Fe(cp)], 89.7 [Ru(cp)], 52.8 ($=CH_2$),[b] 46.7 (CH_2),[b] 1.0 ($RuCH_2$)
19b	218.1, 218.0 (FeCO), 196.7, 195.1 (RuCO),[b] 91.9 [Ru(cp)], 87.9 (=CH), 86.7 [Fe(cp)], 49.8 ($=CH_2$),[b] 45.9 (CH_2),[b] 6.1 ($FeCH_2$)
20	92.3 (=CH), 94.4 [W(cp)], 91.1 [Fe(cp)], 54.2 ($=CH_2$), 45.8 (CH_2), −7.5 (WCH_2)

[a] In $CDCl_3$ using $SiMe_4$ as reference standard (δ = 0.00), J values in Hz. Assignments assisted by APT and HETCOR experiments; in some cases M(CO) peaks were not observed. [b] Assignment uncertain.

α-protons of the alkyl group are fluxional above −10 °C. Similar fluxional behaviour has been observed for complex **15**.[30] The ^1H NMR spectrum of complex **17** (at −30 °C) is however more complicated than that of **15**, since, unlike the latter, it has two different groups at each end of the bridging C_3H_5 group. A detailed analysis of this fluxional behaviour will be reported shortly.[31]

Comparing the ^{13}C NMR data for complexes **15** and **17** (see Table 3), it can be seen that those for the iron side of complex **17** are very similar to data for the diiron complex **15**. Both the $FeCH_2$ and $RuCH_2$ peaks of complex **17** are deshielded by 20–21 ppm relative to the corresponding peaks of 7.[10] The data obtained thus clearly suggest that complex **17** has a very similar structure to that of **15** (Fig. 1).

The complexes $[(cp)(OC)_2Fe(C_4H_8)ML_y]$ [ML_y = $Mo(CO)_3(cp)$, $Ru(CO)_2(cp)$ or $W(CO)_3(cp)$] were treated with the trityl salt to give complexes of the type $[(cp)(OC)_2Fe(C_4H_7)ML_y]PF_6$ **18**–**20** respectively. If the trityl salt abstracts one hydride from a β-carbon atom of a transition-metal alkanediyl complex, two possible structures are possible for complexes **18**–**20**. Complex **18** was found to be unstable in both solution and the solid state and thus few data were obtained. Its IR spectrum is however similar to those of **16**, **19** and **20**, and thus supports its proposed formulation. Since the IR ν(CO) spectrum of $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_4H_7)]PF_6$ shows bands at 2073, 2036, 2007 and 1950 cm^{-1},[29] and complex **18** shows bands at 2073, 2038, 2017 and 1922 cm^{-1} (*i.e.* no bands at *ca.* 1950 cm^{-1}), the Fe atom may be π bonded and the Mo atom π bonded to the hydrocarbon chain.

The ^1H and ^{13}C NMR spectra of complex **19** both showed four peaks of approximately equal intensity in the cp region and the ^{13}C NMR spectrum also showed eight peaks assignable to the carbon atoms of the C_4H_7 group. This indicated that the product consisted of a mixture of two complexes, namely $[(cp)(OC)_2Fe(CH_2CHCH_2CH_2)Ru(CO)_2(cp)]PF_6$ **19a** and $[(cp)(OC)_2Fe(CH_2CH_2CHCH_2)Ru(CO)_2(cp)]PF_6$ **19b**. These two structural isomers were not separated. The NMR data indicated that both were present in approximately equal amounts; the reaction of Ph_3CPF_6 with $[(cp)(OC)_2Fe(C_4H_8)Ru(CO)_2(cp)]$ is thus not metalloselective. Comparing the spectral data to those of $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_4H_7)]PF_6$ indicates that complexes **19a** and **19b** have similar structures. Furthermore, **19a** appears to involve an iron atom which is π bonded and a ruthenium atom which is σ bonded to the hydrocarbon chain. Conversely, complex **19b** appears to involve a π bond between ruthenium and σ bond between iron and hydrocarbon chain. Noteworthy is that the chemical shifts assigned to the protons of the π-bonded section of **19a** and the σ-bonded section of **19b** are almost identical to those assigned to the corresponding sections of the complex $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_4H_7)]PF_6$.[29] The reaction of $[(cp)(OC)_2Fe(C_6H_{12})Ru$-

$(CO)_2(cp)]$ with the trityl salt gives a similar mixture of structural isomers of formula $[(cp)(OC)_2Fe(C_6H_{11})Ru(CO)_2(cp)]PF_6$ **21**. The complexes **19** and **21** were significantly more soluble in CH_2Cl_2 and acetone than is **17**, which may be due to their different structures.

In contrast to the spectra of complex **19**, those of **20** show it to consist of a single isomer. Comparison of the IR, ^1H and ^{13}C NMR spectral data for **20** with those of the complexes $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_4H_7)]PF_6$ and $[(cp)(OC)_2Fe(C_4H_8)W(CO)_3(cp)]$ suggests that the hydride was abstracted from the alkanediyl carbon β to Fe, resulting in the Fe atom being π bonded and the W atom still being σ bonded to the hydrocarbon chain (Fig. 2).

Noteworthy in both the ^1H and ^{13}C NMR spectra of complexes **15**–**21** is that the peaks due to the CH group in complexes with structures as shown in Fig. 1 (**15**–**17**) are significantly more deshielded than are the corresponding =CH peaks in complexes with structures as shown in Fig. 2 (**18**–**21**) (^1H NMR: *ca.* δ 6.5 *vs.* *ca.* 5.3. ^{13}C NMR: *ca.* δ 120–127 *vs.* *ca.* 88–92).

Miscellaneous Studies on some Heterobimetallic Alkanediyl Complexes.—Electrophilic cleavage of transition metal–carbon σ bonds, using a variety of reagents, has been widely studied for a number of different metal systems.[32] Halogen cleavage has been found to be useful for both synthetic purposes and for the characterisation of organometallic compounds.[33] Usually, the reaction of halogens with metal–carbonyl alkyl complexes results in the formation of a metal halide and an alkyl halide. Exceptions are reactions, in co-ordinating solvents, of systems where 'CO insertion' into metal–alkyl bonds can proceed readily.[34,35]

The complex $[(cp)(OC)_2Fe(C_5H_{10})Ru(CO)_2(cp)]$ was treated with 1 mol equivalent of I_2 at 0 °C in CH_2Cl_2. Only the expected cleavage products $[Fe(CO)_2(cp)I]$, $[Ru(CO)_2(cp)I]$ and a trace of $I(CH_2)_5I$ were obtained on work-up, as identified by IR and ^1H NMR spectroscopy. Thus no evidence for a metalloselective reaction was obtained under these conditions. Also, no evidence of a cationic species, $[(cp)(OC)_2Fe(C_5H_{10})Ru(CO)_2(cp)]^+$, was obtained, although $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_4H_8)]^+$ was isolated in the reaction of $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_4H_8)]$ with I_2.[18] No analogous cationic product was obtained on the reaction of $[\{Ru(CO)_2(cp)\}_2(\mu\text{-}C_5H_{10})]$ with I_2.[17]

The reaction of a suspension of $[(cp)(OC)_2Fe(C_6H_{12})W(CO)_3(cp)]$, in hexane, with HCl gas at −78 °C gave approximately equal amounts of $[W(CO)_3(cp)Cl]$ and $[Fe(CO)_2(cp)\{(CH_2)_5CH_3\}]$. Since the $(cp)(OC)_3W\text{–}C$ bond is thermodynamically stronger than the $(cp)(OC)_2Fe\text{–}C$ bond,[36] acid cleavage occurring at the W implies that the Fe–C bond is the kinetically more inert. Since no evidence of $[Fe(CO)_2(cp)Cl]$ or $[W(CO)_3(cp)\{(CH_2)_5CH_3\}]$ was found, the reaction of HCl with $[(cp)(OC)_2Fe(C_6H_{12})W(CO)_3(cp)]$ appears to be totally metalloselective.

Attempts to prepare the co-ordinatively unsaturated complex $[(cp)(OC)_2Fe(C_3H_6)Mo(CO)_2(cp)]$ (*i.e.* a complex which may involve a Fe–Mo bond) by heating complex **1** in $[^2H_8]$toluene or treating it with Me_3NO were unsuccessful. Carbon-13 NMR monitoring of the former experiment showed that at between 70 and 100 °C the carbonyl groups bonded to the Mo atom are fluxional. No evidence of fluxionality between the CO groups of Mo and Fe was observed. Work-up of the NMR solution yielded starting material and small quantities of $[\{Fe(CO)_2(cp)\}_2]$ and $[\{Mo(CO)_3(cp)\}_2]$.

Further experiments are underway to explore the scope of metalloselective reactions in these and related heterobimetallic alkanediyl complexes.

Experimental

All reactions were carried out under nitrogen using standard Schlenk-tube techniques. Tetrahydrofuran and hexane were distilled over $LiAlH_4$ or sodium, toluene and xylene over sodium, CH_2Cl_2 over $CaCl_2$ and acetonitrile over P_2O_5. The heterodinuclear alkanediyl complexes[10,11] discussed above, as well as $[\{Mo(CO)_3(cp)\}_2(\mu\text{-}C_4H_8)]$[37] and $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}CH_2CHCH_2)]PF_6$,[27] were prepared by reported procedures. The reaction of $[\{Fe(CO)_2(cp)\}_2(\mu\text{-}C_3H_6)]$ with 1 mol PPh_3 was carried out according to the published procedure.[18] BDH alumina, active neutral, Brockmann grade 1, was deactivated before use. All other reagents were obtained commercially, unless otherwise stated. Melting points were determined on a Kofler hot-stage microscope (Reichert Thermovar) and are uncorrected. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Infrared spectra were recorded on a Perkin Elmer 983 spectrophotometer in solution cells with NaCl or KBr windows, or as Nujol mulls on NaCl plates. Proton NMR spectra were recorded on a Brüker WH90 or a Varian XR200 spectrometer, ^{13}C NMR spectra, as well as correlation spectroscopy (COSY), heteronuclear correlation spectroscopy (HETCOR) and attached proton test (APT) experiments, were recorded on a Varian XR200 instrument. Chemical shifts are reported relative to $SiMe_4$ (δ 0.00) as an internal (WH90) or external (VXR200) reference standard.

Reactions of $[(cp)(OC)_2Fe(C_3H_6)Mo(CO)_3(cp)]$ *in* MeCN.—*With* PPh_3. Complex **1** (0.200 g, 0.431 mmol) and PPh_3 (0.113 g, 0.431 mmol) were dissolved in MeCN (3.5 cm^3). The mixture was stirred at room temperature for 2 h. A yellow *precipitate* started to form after 18 min. It was filtered off to yield $[(cp)(OC)_2Fe\{(CH_2)_3C(O)\}Mo(PPh_3)(CO)_2(cp)]$ **2a** (0.214 g). The compound was recrystallised from CH_2Cl_2–hexane.

With PMe_2Ph. Complex **1** (0.190 g, 0.409 mmol) was dissolved in MeCN (2 cm^3) and a solution of PMe_2Ph (0.058 cm^3, 0.409 mmol) in MeCN (1.5 cm^3) was added. The mixture was stirred at room temperature for 130 min. Evaporation of the solvent under reduced pressure left a dark oil which was taken up in CH_2Cl_2 and transferred to an alumina column. Elution with CH_2Cl_2 gave a broad yellow band which was collected and evaporated to dryness, leaving $[(cp)(OC)_2Fe\{(CH_2)_3C(O)\}Mo(PMe_2Ph)(CO)_2(cp)]$ **2b** as a yellow oil (57%), identified by its IR and NMR spectra only. $\nu_{max}(CO)$ 1999vs, 1938vs, 1839vs and 1608m cm^{-1} (CH_2Cl_2). Attempts to crystallise this product were not successful.

With CO. Complex **1** (0.200 g, 0.431 mmol) was dissolved in MeCN (8 cm^3) and CO gas was bubbled through this solution for 105 min with stirring. Infrared monitoring of the ν(CO) region showed no further change in the spectra of the mixture after 1 h. The solvent was evaporated *in vacuo* leaving a dark yellow oil, the IR spectrum of which [$\nu_{max}(CO)$ 2078w, 2001s, 1943vs, 1902s and 1645w cm^{-1} (CH_2Cl_2)] was consistent with the product being $[(cp)(OC)_2Fe\{(CH_2)_3C(O)\}Mo(CO)_3(cp)]$ **5**. The product was purified from hot hexane under N_2 to give a yellow oil (0.100 g, 47%). This oil was very air-sensitive and further measurements were not performed on it.

Reaction of $[(cp)(OC)_2Fe(C_4H_8)Mo(CO)_3(cp)]$ *with* 1 *mol equivalent of* PPh_3 *or* PMe_2Ph *in thf*.—The complex $[(cp)(OC)_2Fe(C_4H_8)Mo(CO)_3(cp)]$ (0.21 mmol) was dissolved in thf (8 cm^3) and the phosphine (0.21 mmol) added. The solution was stirred at room temperature for 23 h. Evaporation of the solvent *in vacuo* left a yellow oil, which was crystallised from hot hexane. Both products were obtained in very low yield (4%). Proton NMR and IR data were consistent with them being $[(cp)(OC)_2Fe\{(CH_2)_4C(O)\}MoL(CO)_2(cp)]$, L = PPh_3 (yellow solid, m.p. 66–67 °C) or PMe_2Ph (oily yellow solid). For L = PPh_3: $\nu_{max}(CO)$ 1999s, 1938vs, 1851vs and 1607w (br) cm^{-1} (CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.44 (m, 15 H, PPh_3), 5.00 [d, 5 H, (cp)Mo], 4.69 [s, 5 H, (cp)Fe], 3.05 [t, 2 H, $C(O)CH_2$] and 1.55 [m, 6 H, $(CH_2)_3$]. For L = PMe_2Ph: $\nu_{max}(CO)$ 2007s, 1953s, 1929m, 1851vs and 1634w cm^{-1} (hexane); ^1H NMR ($CDCl_3$) δ 7.42

(m, 5 H, PPh), 4.95 [d, 5 H, (cp)Mo], 4.70 [s, 5 H, (cp)Fe], 2.96 [t, 2 H, $MoC(O)CH_2$], 2.48 (m, 2 H, CH_2), 2.24 (m, 2 H, CH_2), 1.88 (d, 6 H, PMe_2) and 1.38 (m, 2 H, CH_2).

Reaction of $[(cp)(OC)_2Fe(C_6H_{12})Mo(CO)_3(cp)]$ **3** *with* PPh_3 *in* MeCN.—Complex **3** (0.240 g, 0.470 mmol) and PPh_3 (0.125 g, 0.470 mmol) were dissolved in MeCN (4.5 cm^3) and the mixture stirred at room temperature for 140 min, after which time an IR spectrum in the ν(CO) region showed all the starting material to have reacted. The solvent was removed under reduced pressure leaving a yellow oil, which was washed with hexane to give $[(cp)(OC)_2Fe\{(CH_2)_6C(O)\}Mo(PPh_3)(CO)_2(cp)]$ **4** as an oily yellow *solid* (0.217 g).

Reactions of $[\{Mo(CO)_3(cp)\}_2(\mu\text{-}C_4H_8)]$ *with* PPh_3 *in* MeCN. —(*a*) 1 *mol equivalent.* The phosphine (0.096 g, 0.366 mmol) was added to a suspension of $[\{Mo(CO)_3(cp)\}_2(\mu\text{-}C_4H_8)]$ (0.199 g, 0.366 mmol) in MeCN (3.5 cm^3). The mixture was allowed to stand for 2.75 h at room temperature. The product was filtered off to give a yellow solid (0.254 g). Both the IR and ^1H NMR spectra imply that it is an approximately 10:7 mixture of $[(cp)(OC)_2(Ph_3P)Mo\{C(O)(CH_2)_4\}Mo(CO)_3(cp)]$ and $[\{Mo(PPh_3)(CO)_2(cp)\}_2\{\mu\text{-}C(O)(CH_2)_4C(O)\}]$ **6**. This ratio of products was supported by the elemental analyses data (Found: C, 59.90; H, 3.70. Calc.: C, 59.00; H, 4.25%).

(*b*) 2 *mol equivalents.* The complex (0.174 g, 0.320 mmol) and PPh_3 (0.170 g, 0.690 mmol) were dissolved in MeCN (4.5 cm^3). The mixture was stirred at room temperature for 15 h. The resulting precipitate was filtered off to afford complex **6** as a yellow *solid* (0.249 g). Analytically pure samples can be obtained on recrystallisation of this solid from CH_2Cl_2–hexane.

Reaction of $[(cp)(OC)_2Fe(C_3H_6)Ru(CO)_2(cp)]$ **7** *with* PPh_3 *in thf.*—Complex **7** (0.270 g, 0.610 mmol) and PPh_3 (0.161 g, 0.610 mmol) were dissolved in thf (9 cm^3) and the mixture was refluxed for 5 d. Evaporation of the solvent *in vacuo* left an orange oily residue which was washed with hexane to remove any unreacted starting material. The product was then dissolved in the minimum of CH_2Cl_2 and transferred to an alumina column made up with hexane. Elution with hexane gave a pale yellow band from which a very small quantity of starting material was recovered (< 1%). Elution with 20% CH_2Cl_2–hexane gave an orange band, which was collected and the solvent removed under reduced pressure. This gave the product which can be recrystallised from either CH_2Cl_2–hexane or diethyl ether–hexane to give $[(cp)(OC)(Ph_3P)Fe\{C(O)(CH_2)_3\}Ru(CO)_2(cp)]$ **8** (0.193 g) as an orange *solid.*

A repeat experiment using complex **7** (0.202 g, 0.460 mmol) and PPh_3 (0.123 g, 0.470 mmol) in refluxing thf (7.6 cm^3) was complete [IR monitoring of the ν(CO) region] after 2 d 23 h.

Reaction of $[(cp)(OC)_2Fe(C_3H_6)W(CO)_3(cp)]$ **9** *with* PPh_3 *in thf.*—Complex **9** (0.176 g, 0.319 mmol) and PPh_3 (0.085 g, 0.324 mmol) were dissolved in thf (6 cm^3). The mixture was refluxed for 64 h. The course of the reaction was followed by IR spectroscopy in the ν(CO) region. Once the reaction was judged complete the solvent was removed *in vacuo*, leaving a yellow solid. This was dissolved in the minimum of CH_2Cl_2 and transferred to an alumina column made up with hexane. Elution with 20% CH_2Cl_2–hexane gave a pale yellow band from which the solvent was evaporated under reduced pressure to leave a yellow oil. This was identified as unchanged starting material, **9**. Elution with 50% CH_2Cl_2–hexane gave an orange band, which, on evaporation under reduced pressure, gave a yellow *solid* (68%), identified as $[(cp)(OC)(Ph_3P)Fe\{C(O)(CH_2)_3\}W(CO)_3(cp)]$ **10**.

Reaction of $[(cp)(OC)_2Fe(C_3H_6)Re(CO)_5]$ **11** *with* 1 *mol equivalent of* PPh_3 *in thf.*—Complex **11** (0.160 g, 0.293 mmol) was dissolved in thf (5 cm^3) and PPh_3 (0.078 g, 0.297 mmol) was added. The mixture was refluxed for 70.5 h. IR monitoring of the reaction showed very little change in the spectrum of the ν(CO) region after *ca.* 24 h. The solvent was evaporated under reduced pressure to leave a yellow-orange oily solid. This was dissolved in the minimum of CH_2Cl_2 and transferred to an alumina column made up with hexane. Elution with hexane gave a yellow band which, on concentration and cooling to −78 °C, gave a fine pale yellow *solid* identified as $[(cp)(OC)(Ph_3P)Fe\{C(O)(CH_2)_3\}Re(PPh_3)(CO)_4]$ **13** (0.02 g). Elution with 50% CH_2Cl_2–hexane gave an orange band. Evaporation of the solvent under reduced pressure gave an oily orange *solid* identified as $[(cp)(OC)_2Fe(C_3H_6)Re(PPh_3)(CO)_4]$ **12** (0.142 g).

Reactions with Ph_3CPF_6.—$[(cp)(OC)_3Mo(C_4H_8)Mo(CO)_3(cp)]$. The complex $[(cp)(OC)_3Mo(C_4H_8)Mo(CO)_3(cp)]$ (0.191 g, 0.350 mmol) was dissolved in CH_2Cl_2 (6 cm^3). A solution of Ph_3CPF_6 (0.146 g, 0.380 mmol) in CH_2Cl_2 (4 cm^3) was added and the mixture allowed to stand at room temperature for 23 h. A dark blue precipitate formed during this period, which was filtered off (0.055 g) and washed with ether. It was insoluble in CH_2Cl_2 but dissolved in acetone to give an orange solution (which rapidly turned black). The solvent was removed under reduced pressure to give a yellow solid contaminated with a fine blue impurity. The IR spectrum [ν_{max}(CO) 2011m, 1935s, 1903s and 1670w (br) cm^{-1} (Nujol)] was consistent with the product being $[(cp)(OC)_3Mo(C_4H_7)Mo(CO)_3(cp)]PF_6$, but it was contaminated with finely divided metal and/or oxides and attempts to purify it were unsuccessful.

Complexes **1**, **7** *and* $[(cp)(OC)_2Fe(C_4H_8)W(CO)_3(cp)]$. The heterobimetallic complex (0.5 mmol) was dissolved in CH_2Cl_2 (2 cm^3) and a solution of Ph_3CPF_6 (0.6 mmol) in CH_2Cl_2 (4 cm^3) was added. The mixture was allowed to stand at room temperature (reaction times in parentheses). The product precipitated from the reaction solution and was filtered off, recrystallised from acetone–hexane and washed with ether. Thus $[(cp)(OC)_2Fe(C_3H_5)Mo(CO)_3(cp)]PF_6$ **16** was obtained as lustrous golden platelets (77 h), $[(cp)(OC)_2Fe(C_3H_5)Ru(CO)_2(cp)]PF_6$ **17** as orange needles (4 h), and $[(cp)(OC)_2Fe(C_4H_7)W(CO)_3(cp)]PF_6$ **20** as a yellow solid (77 h).

$[(cp)(OC)_2Fe(C_4H_8)Mo(CO)_3(cp)]$ *and* $[(cp)(OC)_2Fe(C_nH_{2n})Ru(CO)_2(cp)]$ (*n* = 4 *or* 6). The heterobimetallic complex (0.33 mmol) was dissolved in CH_2Cl_2 (2 cm^3) and a solution of Ph_3CPF_6 (0.41 mmol) in CH_2Cl_2 (4 cm^3) added. The solution was allowed to stand at room temperature (reaction times and percentage yields in parentheses). The product was precipitated by adding ether, filtered off and washed with ether and hexane. Thus complex **18** was obtained as an orange solid (48 h, 26%) identified only by its IR spectrum ν_{max}(CO) 2073m, 2038m, 2017m and 1922m cm^{-1} (CH_2Cl_2). Complexes **19** and **21** were isolated as yellow solids after reaction times of 8.5 and 24 h respectively.

Reaction of $[(cp)(OC)_2Fe(C_6H_{12})W(CO)_3(cp)]$ *with* HCl *Gas.*—A suspension of $[(cp)(OC)_2Fe(C_6H_{12})W(CO)_3(cp)]$ in hexane was allowed to stand under an atmosphere of HCl gas at −78 °C for *ca.* 2 h, during which time the mixture changed from yellow to orange. The solvent was evaporated under reduced pressure, the product dissolved in the minimum of hexane and transferred to an alumina column made up with hexane. Elution with hexane gave a yellow solution which yielded a yellow oil on evaporation under reduced pressure. The IR, ^1H and ^{13}C NMR spectra of this product (obtained in 25% yield) were identical to those of a freshly prepared sample of $[Fe(CO)_2(cp)\{(CH_2)_5CH_3\}]$.[38] Elution of the column with CH_2Cl_2 gave an orange solution which, on evaporation under reduced pressure, gave $[W(CO)_3(cp)Cl]$ (identified by IR and ^1H NMR spectroscopy) in 22% yield.

Reaction of $[(cp)(OC)_2Fe(C_5H_{10})Ru(CO)_2(cp)]$ *with* I_2.—The complex $[(cp)(OC)_2Fe(C_5H_{10})Ru(CO)_2(cp)]$ (0.89 g, 0.17 mmol) was dissolved in CH_2Cl_2 (2 cm^3). A solution of I_2 (0.044 g, 0.17 mmol) in CH_2Cl_2 (8 cm^3) was added at 0 °C. The solution was stirred at 0 °C for 10 min. Evaporation of the solvent *in vacuo* left a purple solid which was dissolved in CH_2Cl_2 and transferred to an alumina column made up in hexane. Elution with hexane separated two yellow bands, whilst elution with 10% CH_2Cl_2–hexane gave a third yellow solution. Evaporation of the solvents under reduced pressure gave orange oily solids which were identified (by IR and ^1H NMR spectroscopy) as mixtures of $[Fe(CO)_2(cp)I]$[39] and $[Ru(CO)_2(cp)I]$[40] in differing ratios. A trace of $I(CH_2)_5I$ was also observed (^1H NMR spectroscopy). No other products could be isolated.

Acknowledgements

We thank the Foundation for Research Development and the University of Cape Town for support, Johnson Matthey and PGM Chemicals for generous loans of ruthenium trichloride and Professor Graham Jackson for helpful discussion.

References

1 J. Breimair, B. Niemer, K. Raab and W. Beck, *Chem. Ber.*, 1991, **124**, 1059 and refs. therein.
2 C. P. Casey and J. D. Audett, *Chem. Rev.*, 1986, **86**, 339; J. R. Moss and L. G. Scott, *Coord. Chem. Rev.*, 1984, **60**, 171.
3 G. J. Arsenault, M. Crespo and R. J. Puddephatt, *Organometallics*, 1987, **6**, 2255.
4 W. Beck and B. Olgemöller, *J. Organomet. Chem.*, 1977, **127**, C45.
5 K. Raab, U. Nagel and W. Beck, *Z. Naturforsch., Teil B*, 1983, **38**, 1466.
6 B. Olgemöller and W. Beck, *Chem. Ber.*, 1981, **114**, 867.
7 W. Beck, *Polyhedron*, 1988, **7**, 2255.
8 W. Kaminsky and H. Sinn, *Liebigs Ann. Chem.*, 1975, 424.
9 M. Cook, N. J. Forrow and S. A. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1983, 2435.
10 H. B. Friedrich, J. R. Moss and B. K. Williamson, *J. Organomet. Chem.*, 1990, **394**, 313.
11 S. J. Archer, K. P. Finch, H. B. Friedrich, J. R. Moss and A. M. Crouch, *Inorg. Chim. Acta*, 1991, **182**, 142.
12 I. S. Butler, F. Basolo and R. G. Pearson, *Inorg. Chem.*, 1967, **6**, 2074.
13 M. Green and D. J. Westlake, *J. Chem. Soc. A*, 1971, 367.
14 A. Wojcicki, *Adv. Organomet. Chem.*, 1973, **11**, 87.
15 M. L. H. Green, L. C. Mitchard and M. G. Swanwick, *J. Chem. Soc. A*, 1971, 794.
16 J. A. S. Howell and A. J. Rowan, *J. Chem. Soc., Chem. Commun.*, 1979, 484; *J. Chem. Soc., Dalton Trans.*, 1980, 1845.
17 K. P. Finch, M. A. Gafoor, S. F. Mapolie and J. R. Moss, *Polyhedron*, 1991, **10**, 963.
18 J. R. Moss and L. G. Scott, *J. Organomet. Chem.*, 1989, **363**, 351.
19 F. Calderazzo, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 299.
20 E. J. Kuhlman and J. J. Alexander, *Coord. Chem. Rev.*, 1980, **33**, 195.
21 L. G. Scott, M.Sc. Thesis, University of Cape Town, 1984.
22 S. F. Mapolie, Ph.D. Thesis, University of Cape Town, 1989.
23 P. Johnston, G. J. Hutchings and N. J. Coville, *J. Am. Chem. Soc.*, 1989, **111**, 1902.
24 J. I. Seeman and S. G. Davies, *J. Am. Chem. Soc.*, 1985, **107**, 6522.
25 S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton and M. Whittaker, *J. Am. Chem. Soc.*, 1987, **109**, 5711 and refs. therein.
26 T. C. Flood, F. J. Dissanti and D. L. Miles, *Inorg. Chem.*, 1976, **15**, 1910.
27 R. B. King and M. B. Bisnette, *J. Organomet. Chem.*, 1967, **7**, 311.
28 M. Laing, J. R. Moss and J. Johnson, *J. Chem. Soc., Chem. Commun.*, 1977, 656.
29 J. W. Johnson and J. R. Moss, *Polyhedron*, 1985, **4**, 563.
30 G. E. Jackson, J. R. Moss and L. G. Scott, *S. Afr. J. Chem.*, 1983, **36**, 69.
31 S. J. Archer, H. B. Friedrich, M. A. Gafoor, A. T. Hutton and J. R. Moss, unpublished work.
32 M. D. Johnson, *Acc. Chem. Res.*, 1978, **11**, 57.
33 G. W. Parshall and J. J. Mrowca, *Adv. Organomet. Chem.*, 1968, **7**, 157.
34 S. F. Mapolie and J. R. Moss, *J. Chem. Soc., Dalton Trans.*, 1990, 299.
35 S. P. Nolan, R. L. de la Vega and C. D. Hoff, *J. Organomet. Chem.*, 1986, **315**, 187.
36 C. Mancuso and J. Halpern, *J. Organomet. Chem.*, 1992, **428**, C8.
37 H. Adams, N. A. Bailey and M. J. Winter, *J. Chem. Soc., Dalton Trans.*, 1984, 273.
38 A. Emeran, M. A. Gafoor, J. K. I. Goslett, Y.-H. Liao, L. Pimble and J. R. Moss, *J. Organomet. Chem.*, 1991, **405**, 237.
39 T. E. Sloan and A. Wojcicki, *Inorg. Chem.*, 1968, **7**, 1268.
40 R. J. Haines and A. L. du Preez, *J. Chem. Soc., Dalton Trans.*, 1972, 944.

Received 23*rd February* 1993; *Paper* 3/01078C