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REACTIONS OF TRANSITION METAL σ-ACETYLIDE COMPLEXES

IX *. PREPARATION AND PROPERTIES OF SOME CYCLOHEPTATRIENYLVINYLIDENE COMPLEXES

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Summary

Addition of $[C_7H_7][PF_6]$ to iron, ruthenium or osmium alkynyl complexes has given eight cationic cycloheptatrienylvinylidene derivatives $[M\{C{=}C(C_7H_7)R\}(L)_2(\eta\text{-}C_5H_5)][PF_6]$ (M = Fe, Ru or Os; R = Me, Pr, Ph or C_6F_5; L = PPh_3, L_2 = dppm or dppe; but not all combinations). With $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$, only $[Fe(CO)_2(thf)(\eta\text{-}C_5H_5)][PF_6]$ was obtained. Reactions of the new complexes are characterised by loss of the C_7H_7 group. The NMR spectra and FAB mass spectra are described in detail.

Introduction

A useful synthetic route to mononuclear vinylidene complexes is the addition of electrophilic reagents to metal acetylide complexes [1]. This reaction has been most usefully employed with protic sources [2] or alkylating agents such as $[R_3O][BF_4]$ (R = Me or Et), FSO_3Me [2,3], and alkyl halides [4], and the reactions are an experimental confirmation of the theoretical prediction that electron density in the HOMO of the metal acetylide is concentrated on the β-carbon of the acetylide function [5]. Recently, we briefly described the use of other types of electrophiles in this reaction, including halogens [6], aryldiazonium and tropylium cations [7]; this paper describes our studies of the products of the latter reaction in detail.

Results and discussion

Addition of a solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ in dichloromethane to a suspension of $[C_7H_7][PF_6]$ in the same solvent produced a red solution; work-up

* For part VIII, see ref. 18.

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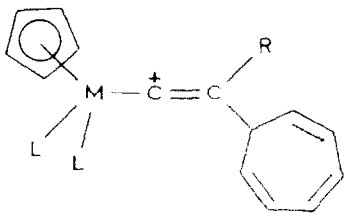


	M	L_2	R
1	Ru	$(PPh_3)_2$	Ph
2	Ru	dppm	Ph
3	Ru	dppe	Ph
4	Ru	$(PPh_3)_2$	C_6F_5
5	Ru	$(PPh_3)_2$	Me
6	Ru	$(PPh_3)_2$	Pr
7	Os	$(PPh_3)_2$	Ph
8	Fe	dppe	Ph

afforded orange crystals of $[Ru\{C{=}CPh(C_7H_7)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (**1**) in high yield. Similar air-stable complexes were obtained from $Ru(C_2R)(L)_2(\eta\text{-}C_5H_5)$ (R = Ph, L_2 = dppm (**2**), dppe (**3**); L = PPh_3, R = C_6F_5 (**4**), Me (**5**), Pr (**6**)), $Os(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (**7**) and $Fe(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ (**8**). These compounds were characterised by elemental microanalysis, various spectroscopic studies, and in one case, a single-crystal X-ray study. They are insoluble in light petroleum, diethyl ether, and water, slightly soluble in methanol and ethanol, more soluble in tetrahydrofuran, acetone and chloroform, and very soluble in dichloromethane and dimethyl sulphoxide.

The IR spectra are characterised by medium to strong absorptions between 1640–1650 cm^{-1} arising from the C=C double bonds of the vinylidene and cycloheptatrienyl groups, and strong broad ν(PF) bands at ca. 840 cm^{-1} from the PF_6^- anion. The ^1H NMR spectra contain sharp singlets between δ 5.2–6.2 assigned to the C_5H_5 protons, and three multiplets between δ 5.0–7.0 assigned to six vinylic protons (three sets of two equivalent nuclei each) of the cycloheptatrienyl group. The remaining proton resonates between δ 2.2–3.2 and is coupled to two of the vinyl protons, thus appearing as a triplet. In some cases, overlapping signals from the tertiary phosphine ligands (dppm and dppe) prevent observation of all three signals (see Experimental). The phenyl protons are found in the usual aromatic region, between δ 7–8.

^{13}C NMR spectra were obtained only for **1**, **4**, **5** and **7**, the other complexes being too insoluble in common deuterated solvents for spectra to be obtained. The methine carbon of the C_7H_7 group resonates between δ 32.7–38.2, the lowest-field signal being found for the C_6F_5 complex (**4**), in which the fluoroaromatic group

deshields the methine carbon by inductive electron withdrawal. The three sets of signals from the vinylic carbons were found between δ 124–126 and 131–133, and were assigned, together with the methine resonance, by off-resonance decoupling experiments. The phenyl resonances were found as multiplets between δ 125–138 and exhibited splitting patterns consistent with coupling to two ^{31}P nuclei. The C_5H_5 resonances were singlets between δ 93–96, while the metal-bonded carbon in **1** gave a triplet at δ 347, the low-field chemical shift being consistent with the extremely electron-deficient nature of this carbon, and similar to those found for other vinylidene complexes. The β-carbon resonance was not conclusively identified as it lies under the phenyl multiplets.

The X-ray structure of **3** has been described earlier [7]. The Ru C distance of 1.848(9) Å is considerably shorter than that in $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (2.016(3) Å) [8], and is consistent with efficient back-bonding from the metal into an orbital on the vinylidene ligand. The C=C bond length (1.32(1) Å) implies a bond order of ca. two, and is similar to those of the localised C=C bonds in the C_7 ring (1.294(16)–1.315(14) Å). The Ru–C(33)–C(34) system is almost linear (174.9(6)°). The X-ray structure confirms the presence of the non-planar, tub-shaped cycloheptatrienyl group, and the (calculated) location of the proton attached to the methine carbon, pointing to the centre of one of the phenyl rings of the dppe ligand, is interesting. Steric congestion in **3** is reduced by the almost orthogonal arrangement of the phenyl ring planes.

FAB mass spectra

The technique of fast atom bombardment mass spectrometry is well suited to the study of ionic organometallic complexes, and we have measured the spectra of complexes **3**, **4**, **8** and **9**. In the former, the ion at highest *m/z* corresponds to the cation (hereafter referred to as $[M]^+$) with a molecule of matrix added. The molecular cation fragments by competitive loss of the two vinylidene substituents; loss of $C_7H_7^{\cdot}$ is favoured, this ion (corresponding to the molecular ion of the parent acetylide) is the base peak in **8**. Further breakdown of this ion (*m/z* 620) involves loss of the phenylacetylide group to give $[Fe(dppe)(C_5H_5)]^+$. An unusual loss of C_5H_6 from this ion gives $[Fe\{C_2H_3(PPh_2)_2\}]^+$, which can be formulated as containing a 5e donor $[C_2H_3(PPh_2)_2]^-$ ligand. Other breakdown routes include elimination of C_6H_6 or C_2H_4 molecules; at lower *m/z*, ions containing the PPh_2^+, CH_2PPh_2, and $C_2H_2PPh_2$ fragments attached to the $Fe(C_5H_5)$ moiety are found. Fragmentation of the ruthenium analogue **3** proceeds more cleanly: while loss of $C_7H_7^{\cdot}$ and $C_6H_5^{\cdot}$ from $[M]^+$ are both found, the base peak is $[Ru(dppe)(C_5H_5)]^+$, which then loses PPh_2 and C_2H_4.

In the spectrum of complex **4**, $[M]^+$ fragments by loss of $C_7H_7^{\cdot}$ (major), PPh_3 or $F^{\cdot}$ (minor). The base peak is $[Ru(PPh_3)(C_5H_5)]^+$, which loses Ph$^{\cdot}$, $C_5H_5^{\cdot}$ or PPh groups. Also prominent are the parent acetylide ion which loses Ph$^{\cdot}$, and *m/z* 448, formed by transfer of fluorine to the metal (with elimination of $C_2C_6F_4$). Several ions (e.g. *m/z* 989, 898) appear to contain oxygen, perhaps as a result of oxidation.

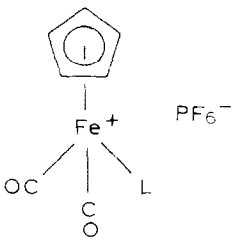
Reactions

One of the most interesting aspects of the chemistry of vinylidene complexes has been the elaboration of the vinylidene ligand and its conversion to carbene or carbyne ligands, for example, or its reactions with other nucleophilic reagents to

give substituted vinyl complexes. Following the synthesis of the complexes described above, we attempted to convert them into further examples of cycloheptatrienyl-substituted carbenes, vinyls or acyls. In all these reactions, we were uniformly unsuccessful, ready displacement of the C_7 group occurring, probably as the appropriately substituted cycloheptatriene. Thus addition of sodium methoxide afforded the parent acetylide complex, and we obtained mass spectral evidence for a species showing a parent ion at m/z 122 (calculated for C_7H_7OMe, 122) although we were not able to isolate this compound in a pure state. Similarly, attempts to add hydride (using $K[BHBu^s_3]$) or methanol to **1**, or water to **3**, gave respectively $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$, $[Ru\{C(OMe)CH_2Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ and $[Ru(CO)(dppe)(\eta\text{-}C_5H_5)]^+$, formed by displacement of the C_7 group from the cycloheptatrienylvinylidene complexes, followed in the latter cases by subsequent transformation of the acetylide in the presence of a trace of acid generated in the reaction, or present in the tropylium salt despite precautions taken to dry this material in vacuo. The observed reactions presumably result from the high stability of the $[C_7H_7]^+$ cation and its consequent ready displacement.

Related chemistry

A reaction between $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ and $[C_7H_7][PF_6]$ afforded $[Fe(CO)_2(thf)(\eta\text{-}C_5H_5)][PF_6]$ (**9**) as a red precipitate after extended stirring in tetrahydrofuran. In the original synthesis of this cation the tetrafluoroborate salt was formed by Lewis acid ($AgBF_4$) removal of iodine from $FeI(CO)_2(\eta\text{-}C_5H_5)$ in thf solution [9]. The mechanism of formation using $[C_7H_7][PF_6]$ appears to involve



(**9**, L = thf ;

10, L = CO)

intial formation of a cycloheptatrienyl-vinylidene. FAB-MS analysis of the reaction mixture after 1 h using a CH_3CN/CH_2Cl_2 solvent system, indicated the presence of $[Fe\{C{=}CPh(C_7H_7)\}(CO)_2(\eta\text{-}C_5H_5)]^+$ (m/z 369). This complex then loses the organic fragment in tetrahydrofuran, presumably through nucleophilic attack on the α-carbon. As the organic fragment has not been isolated it is not possible to say more about the mechanism. It is known that vinylidene complexes containing the $Fe(CO)_2(\eta\text{-}C_5H_5)$ group are exceedingly reactive, and much less stable than complexes containing the $Ru(PR_3)_2(\eta\text{-}C_5H_5)$ group [1].

Attempted crystallisation of **9** from acetone/EtOH resulted in isolation of $[Fe(CO)_3(\eta\text{-}C_5H_5)][PF_6]$ (**10**) [10] in low yield. The cation in **9** is known to exchange its tetrahydrofuran readily, and carbonylation occurs under mild conditions [11]. In acetone the complex $[Fe(CO)_2(acetone)(\eta\text{-}C_5H_5)]^+$ is formed rapidly; the coordinated acetone is also readily replaced by CO, and in solution exchanges with the

bulk solvent as shown by an NMR study [12]. From our results it appears $[Fe(CO)_2(acetone)(\eta\text{-}C_5H_5)]^+$ either undergoes an intramolecular elimination or is involved in intermolecular CO exchange. This has been noted previously: in the original synthesis of $[Fe(CO)_3(\eta\text{-}C_5H_5)]^+$ a control reaction involving treatment of $FeCl(CO)_2(\eta\text{-}C_5H_5)$ with $Na[BPh_4]$ in acetone also resulted in the formation of the tricarbonyl complex (12% after 6 days) [13].

Conclusion

Kinetically stable cycloheptatrienylvinylidene complexes have been obtained from reactions between selected iron, ruthenium, and osmium acetylide complexes and tropylium salts. Ready displacement of the C_7H_7 fragment occurs on attempted reactions designed to further elaborate the new vinylidene ligand. Formation of a substituted vinylidene appears to occur in the reaction between $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ and tropylium cation, but displacement of the vinylidene group occurs in tetrahydrofuran, resulting in the formation of $[Fe(CO)_2(thf)(\eta\text{-}C_5H_5)][PF_6]$ as the isolated product.

Experimental

General conditions

All reactions were run under nitrogen; except for the reaction of $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$, no special precautions were taken to exclude air during work-up, since most complexes proved to be stable in air as solids, and for short times in solution. Solvents were dried and distilled under nitrogen before use.

Instrumentation

IR, Perkin–Elmer 683 double-beam; NMR, Bruker WP80E (^1H at 80MHz, ^{13}C at 20.1 MHz) or Bruker CXP300 (^1H at 300 MHz, ^{13}C at 75.4 MHz); mass spectra, VG ZAB2 HF with FAB probe. Argon was used as the exciting gas, with source pressures typically 10^{-6} mbar; FAB gun voltage 7.5 keV, current 1 mA, ion accelerating potential 8 kV.

Precursors

Tropylium hexafluorophosphate from Cationics, Inc., Cleveland, Ohio. Literature methods were used to make $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ [15], $Ru(C_2R)(L)_2(\eta\text{-}C_5H_5)$ (R = Ph, L_2 = dppm, dppe; L = PPh_3, R = C_6F_5, Me, Ph) [16], $Os(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ [16] and $Fe(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ [4].

Preparation of cycloheptatrienylvinylidene complexes

(a) [Ru{C=CPh(C$_7$H$_7$)}(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (1). A solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (1000 mg, 1.26 mmol) in CH_2Cl_2 (10 ml) was added to a suspension of vacuum-dried $[C_7H_7][PF_6]$ (300 mg, 1.27 mmol) in CH_2Cl_2 (10 ml), immediately giving a red solution, which was stirred for 20 min, and then evaporated to dryness. The residue was extracted with CH_2Cl_2 (5 ml), and the extract filtered into excess stirred ether to give a bright orange precipitate. Crystallisation (CH_2Cl_2/EtOH) gave orange crystals of $[Ru\{C{=}CPh(C_7H_7)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (**1**) (1051 mg, 81%), m.p. 170°C (dec) (Found: C, 65.56; H, 4.66; $C_{56}H_{47}F_6P_3Ru$ calc: C, 65.43; H, 4.61%). Infrared (Nujol): ν(C=C) 1670s, ν(PF)

840vs(br) cm^{-1}; other bands at 1610w, 1593w, 1575w, 1480s, 1435s, 1395w, 1315w, 1184w, 1160w, 1090s, 1071w, 1020w, 1000m, 875m, 750(sh), 741m, 718m, 698s, 645w cm^{-1}. ^1H NMR: δ [$(CD_3)_2CO$] 2.85 (t, J(HH) 11 Hz, 1H, CH), 5.25 (s, 5H, C_5H_5), 5.34 (m, 2H, =CH), 6.28 (m, 2H, =CH), 6.53 (m, 2H, =CH), 7.0–7.6 (m, 35H, C_6H_5). ^{13}C NMR: δ [$(CD_3)_2CO$] 36.42 (s, CH), 94.44 (s, C_5H_5), 123.99 (s, =CH), 125.48 (s, =CH), 132.68 (s, =CH), 128–134 (m, C_6H_5), 346.95 (t, J(CP) 16 Hz, RuC).

(b) [Ru{C=CPh(C$_7$H$_7$)}(dppm)(η-C$_5$H$_5$)][PF$_6$] (2). This complex was prepared as in (a) above from Ru(C_2Ph)(dppm)(η-C_5H_5) (101 mg, 0.15 mmol) and [C_7H_7][PF_6] (44 mg, 0.19 mmol), as orange crystals (96 mg, 72%), m.p. 181–182 °C (Found: C, 60.50; H, 4.55; $C_{48}H_{39}F_6P_3Ru$ calc: C, 60.88; H, 4.43%). Infrared: ν(C=C) 1647s, ν(P–F) 840vs(br); other bands at 1615w, 1598w, 1449s, 1270s, 1238w, 1215w, 1190w, 1155w, 1100m, 1028w, 1015w, 1000w, 985w, 875m, 772w, 752w, 748w, 736(sh), 730w, 719m, 702m, 692s, 645w cm^{-1}. ^1H NMR: δ [$(CD_3)_2CO$] 2.23 (t, J(HH) 5.4 Hz, 1H, CH), 5.18 (m, 2H, CH_2), 5.79 (m, 2H, =CH), 6.12 (s, 5H, C_5H_5), 6.37 (m, 2H, =CH), 6.97 (m, 2H, =CH), 7.1–7.8 (m, 25H, C_6H_5).

(c) [Ru{C=CPh(C$_7$H$_7$)}(dppe)(η-C$_5$H$_5$)][PF$_6$] (3). This complex was prepared as in (a) above, from Ru(C_2Ph)(dppe)(η-C_5H_5) (800 mg, 1.20 mmol) and [C_7H_7][PF_6] (350 mg, 1.48 mmol), as rose-pink crystals (1030mg, 95%) m.p. > 132 °C (dec) (Found: C, 60.34; H, 4.61; $C_{46}H_{41}F_6P_3Ru$ calc: C, 61.27; H, 4.58%). Infrared: ν(C=C) 1537m, ν(P–F) 840vs(br) cm^{-1}; other bands at 1610w, 1594m, 1574w, 1492(sh), 1480s, 1439s, 1418w, 1390w, 1368w, 1310w, 1186w, 1100m, 1072w, 1050w, 1028w, 1017w, 1000w, 928w, 878m, 775m, 765(sh), 745m, 730s, 705s, 692s, 680(sh), 651m, 645m cm^{-1}. ^1H NMR: δ [$(CD_3)_2CO$] 3.27 (m, 5H, CH_2 and CH), 5.00 (m, 2H, =CH), 5.87 (s, 5H, C_5H_5), 5.90 (m, 2H, =CH), 6.26 (m, 2H, =CH), 6.93–7.60 (m, 25H, Ph).

(d) [Ru{C=C(C$_6$F$_5$)(C$_7$H$_7$)}(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (4). A solution of Ru($C_2C_6F_5$)(PPh_3)$_2$(η-C_5H_5) (400 mg, 0.454 mmol) in dry thf (10 ml) was added to a suspension of vacuum-dried [C_7H_7][PF_6] (128 mg, 0.542 mmol) in dry thf (10 ml) giving an orange solution. The reaction mixture was stirred for 60 min and concentration to ca. 2 ml afforded an orange powder. The addition of five drops of diethyl ether to the mother liquor and refrigeration at −30 °C yielded a second crop of [Ru{C=C(C_6F_5)(C_7H_7)}(PPh_3)$_2$(η-C_5H_5)][PF_6] (**4**). Recrystallisation (Me_2CO/EtOH) gave orange crystals (375 mg, 74%), m.p. > 127 °C (dec) (Found: C, 59.93; H, 4.06; $C_{56}H_{42}F_{11}P_3Ru$ calc: C, 59.84; H, 4.30%). Infrared: ν(C=C) 1650s, ν(P–F) 840vs(br) cm^{-1}; other bands at 1695w, 1611w, 1590w, 1575w, 1519s, 1490s, 1436s, 1368(sh), 1312w, 1190w, 1159w, 1138w, 1096(sh), 1090m, 1069m, 1000w, 981s, 940w, 930w, 899w, 871(sh), 860s, 823s, 772m, 742s, 710(sh), 690s cm^{-1}. ^1H NMR: δ [$(CD_3)_2CO$] 3.19 (t, J(HH) 9 Hz, 1H, CH), 5.29 (s, 5H, C_5H_5), 5.58 (m, 2H, =CH), 6.56 (m, 2H, =CH), 6.75 (m, 2H, =CH), 7.23–7.75 (m, 30H, C_6H_5). ^{13}C NMR: δ($CDCl_3$) 38.16 (s, CH), 95.80 (s, C_5H_5), 122.25 (s, =CH), 126.00 (s, =CH), 131.80 (s, =CH), 128–138 (m, C_6H_5), 337.29 (t, J(CP) 13 Hz, RuC).

(e) [Ru{C=CMe(C$_7$H$_7$)}(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (5). A solution of Ru(C_2Me)(PPh_3)$_2$(η-C_5H_5) (200 mg, 0.27 mmol) in diethyl ether (10 ml) and dichloromethane (10 ml) was treated with a suspension of [C_7H_7][PF_6] (excess) in diethyl ether. The yellow solution immediately became an orange suspension. After stirring for 15 min, the solvent was removed in vacuo. A dichloromethane extract of the residue was filtered; addition of methanol to the filtrate and concentration afforded orange

crystals of $[Ru\{C{=}CMe(C_7H_7)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (**5**) (228 mg, 86%), m.p. 95–98°C (dec). (Found: C, 63.2; H, 4.6; $C_{51}H_{45}F_6P_3Ru$ calc: C, 63.4; H, 4.7%). Infrared (Nujol): ν(CC) 1682m; ν(PF) 836s(br); other bands at 1609w, 1589w, 1572w, 1435m, 1315w, 1187w, 1160w, 1090m, 1033w, 996w, 875w, 756w, 741m, 692s cm^{-1}. ^1H NMR: δ ($CDCl_3$) 1.90 (s, 3H, Me), 2.34 (t, J(HH) 5 Hz, 1H, CH), 5.09 (s, 5H, C_5H_5), 5.25 (m, 2H, =CH), 6.25 (m, 2H, =CH), 6.48 (m, 2H, =CH), 7.33 (m, 30H, Ph). ^{13}C NMR: δ ($CDCl_3$) 19.6 (CH_3), 34.4 (CH), 93.6 (C_5H_5), 119.7 (RuC=C), 122.0, 122.8, 125.2 (=C), 128.3–136.1 (Ph), 352.4 (t, J(CP) 17 Hz, RuC).

(f) [Ru{C=CPr(C₇H₇)}(PPh₃)₂(η-C₅H₅)][PF₆] (6). This complex was prepared as a diethyl ether solvate as in (a) above, from $Ru(C_2Pr)(PPh_3)_2(\eta\text{-}C_5H_5)$ (226 mg, 0.30 mmol) and $[C_7H_7][PF_6]$ (82 mg, 0.35 mmol), as a buff powder on precipitation from excess stirred diethyl ether (264 mg, 89%), m.p. > 110°C (dec) (Found: C, 62.35; H, 5.67. $C_{53}H_{47}F_6P_3Ru \cdot C_4H_{10}O$ calc: C, 64.22; H, 5.39%). Infrared: ν(C=C) 1668m, ν(PF) 840vs(br) cm^{-1}; other bands at 1610w, 1588w, 1572w, 1435s, 1295w, 1240w, 1178w, 1155w, 1115m, 1090s, 1028w, 1015w, 1009w, 999w, 971m, 701m, 692m, 665(sh), 655(sh), 645s cm^{-1}. ^1H NMR: δ ($CDCl_3$) 0.92 (t, J(HH), 6.8 Hz, 3H, $CH_2CH_2CH_3$), 1.21 (t, J(HH) 7 Hz, 6H, $(CH_3CH_2)_2O$), 1.58 (m, 2H, $CH_2CH_2CH_3$), 2.28 (m, 3H, CH and $CH_2CH_2CH_3$), 3.48 (s, J(HH) 7 Hz, 4H, $(CH_3CH_2)_2O$), 5.10 (s, 5H, C_5H_5), 5.27 (m, 2H, =CH), 6.28 (m, 2H, =CH), 6.43 (m, 2H, =CH), 6.8–7.5, (m, 30H, C_6H_5).

(g) [Os{C=CPh(C₇H₇)}(PPh₃)₂(η-C₅H₅)][PF₆] (7). The reaction between $[C_7H_7][PF_6]$ (77 mg, 0.33 mmol) and $Os(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (260 mg, 0.30 mmol) analogously gave $[Os\{C{=}CPh(C_7H_7)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (**7**) as red-pink crystals (273 mg, 83%) m.p. > 206°C (dec) (Found: C, 60.03; H, 4.24; $C_{56}H_{47}F_6OsP_3$ calc: C, 60.21; H, 4.24%). Infrared: ν(C=C) 1675s, ν(PF) 840vs(br) cm^{-1}; other bands at 1711w, 1692w, 1655w, 1645w, 1595w, 1575w, 1483(sh), 1448(sh), 1368(sh), 1295w, 1245w, 1180w, 1090m, 1000w, 874(sh), 740m, 720s, 696s, 682(sh) cm^{-1}. ^1H NMR: δ [$(CD_3)_2CO$] 2.64 (t, J(HH) 6 Hz, 1H, CH), 5.43 (s, 5H, C_5H_5), 5.27 (m, 2H, =CH), 6.32 (m, 2H, =CH), 6.46 (m, 2H, =CH), 7.18 (m, 35H, C_6H_5). ^{13}C NMR: δ [$(CD_3)_2CO$] 32.7 (s, CH), 92.79 (s, C_5H_5), 125.1 (s, =CH), 125.6 (s, =CH), 133.1 (s, =CH), 125.8–137.0 (m, C_6H_5).

(h) [Fe{C=CPh(C₇H₇)}(dppe)(η-C₅H₅)][PF₆] (8). A reaction between $Fe(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ (200 mg, 0.32 mmol) and $[C_7H_7][PF_6]$ (100 mg, 0.42 mmol) in thf (10 ml) gave a buff-orange powder of $[Fe\{C{=}CPh(C_7H_7)\}(dppe)(\eta\text{-}C_5H_5)][PF_6]$ (**8**) (217 mg, 78%), m.p. > 155°C (dec) (Found: C, 64.16; H, 4.66; $C_{46}H_{41}F_6FeP_3$ calc: C, 64.50; H, 4.82%). Infrared: ν(C=C) 1665m, ν(PF) 840vs(br); other bands at 1596m, 1578w, 1488m, 1439s, 1100s, 1072w, 1000m, 878s, 795w, 742m, 719s, 711s, 699s, 680m, 645m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 1.91 (t, J(HH) 5 Hz, 1H, CH), 3.10 (m, 4H, PCH_2), 4.99 (m, 2H, =CH), 5.14 (s, 5H, C_5H_5), 5.93 (m, 2H, =CH), 6.19 (m, 2H, =CH), 7.10–7.35 (m, 25H, Ph).

Reactions of cycloheptatrienylvinylidene complexes

(a) Sodium methoxide. A suspension of $[Ru\{C{=}CPh(C_7H_7)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (200 mg, 0.20 mmol) in methanol was treated with 0.93 *M* NaOMe solution (5 drops, excess). A yellow powder precipitated after ca. 5 min. The solvent volume was reduced to 5 ml and the powder collected, washed (MeOH) and dried, to give $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (143 mg, 93%), m.p. 201–203°C (dec) (Lit. [16] 205°C (dec)). Infrared (Nujol): ν(CC) 2065 cm^{-1} (Lit. [16] ν(C≡C) 2068 cm^{-1}).

Similarly, reactions of **2**, **3** and **4** with NaOMe afforded $Ru(C_2Ph)(dppm)(\eta\text{-}C_5H_5)$ (72%), $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ (68%) and $Ru(C_2C_6F_5)(PPh_3)_2(\eta\text{-}C_5H_5)$ (89%), respectively.

(b) Potassium tri-s-butylborohydride (K-Selectride, K[BHBu$^s_3$]). A suspension of $[Ru\{C{=}CPh(C_7H_7)\}(dppe)(\eta\text{-}C_5H_5)][PF_6]$ (126 mg, 0.14 mmol) in thf (10 ml) was treated with 0.5 *M* K-Selectride (0.5 ml of a 0.5 *M* solution in thf, 0.25 mmol) to give an orange solution which after 5 min stirring became yellow. Addition of MeOH (10 ml) and concentration of the solution gave yellow crystals of $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ (82 mg, 88%). The product was identified by comparing its melting point and infrared spectrum with those of an authentic sample.

(c) Methanol. A suspension of $[Ru\{C{-}CPh(C_7H_7)\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (200 mg, 0.195 mmol) in MeOH (20 ml) was heated to reflux point. After 24 h the reaction mixture was purple, a further six days' reflux and loss of solvent by evaporation resulted in a yellow precipitate. This was collected, recrystallised (CH_2Cl_2/MeOH) and identified as $[Ru\{C(OMe)CH_2Ph\}(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (84 mg, 44%) m.p. 175–176 °C (Lit. [17] 182–185 °C). Infrared (Nujol): ν(CO) 1263s, ν(PF) 840vs(br) cm^{-1}, (Lit. [17] 1265s and 840vs(br) cm^{-1}, respectively). ^{1}H NMR: δ ($CDCl_3$) 3.43 (s, 3H, OMe), 4.77 (s, 5H, C_5H_5), 4.98 (s, 2H, CH_2Ph), 7.19 (m, 35H, Ph). (Lit. [12] δ ($CDCl_3$) 3.49 (s, 3H, OMe), 4.84 (s, 5H, C_5H_5), 5.06 (s, 2H, CH_2Ph), 7.31 (m, 35H, Ph).

(d) Water. A solution of $[Ru\{C{=}CPh(C_7H_7)\}(dppe)(\eta\text{-}C_5H_5)][PF_6]$ (200 mg, 0.22 mmol) in aqueous thf (25% v/v) was heated at reflux point for 44 h. The resulting yellow solution was evaporated to dryness, the residue extracted with CH_2Cl_2 and the extract filtered directly into excess stirred diethyl ether. The light yellow precipitate was collected, washed with ether and dried to give $[Ru(CO)(dppe)(\eta\text{-}C_5H_5)][PF_6]$ (129 mg, 79%) (Found: C, 51.31; H, 3.88; $C_{32}H_{27}F_6OP_3Ru$ calc: C, 52.11; H, 3.96%). Infrared (Nujol): ν(CO) 1990s, ν(PF) 840vs(br) cm^{-1}; other bands at 1690w, 1676w, 1438s, 1369(sh), 1310w, 1280(sh), 1198w, 1176w, 1123w, 1100m, 1072w, 1048w, 1000m, 740m, 695s, 679w, 650w cm^{-1}. ^{1}H NMR: δ[$(CD_3)_2CO$] 5.51 (s, 5H, C_5H_5) 7.31–7.96 (m, Ph).

Reaction between $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ and $[C_7H_7][PF_6]$

$[C_7H_7][PF_6]$ (149 mg, 0.63 mmol) was added to a solution of $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ (165 mg, 0.59 mmol) in thf (20 ml). After stirring for 16 h a flocculent red precipitate had formed from the orange solution. This precipitate was collected by filtration and washed with cold thf (2 × 5 ml) and diethyl ether (2 × 5 ml). Recrystallisation (CH_2Cl_2/diethyl ether) afforded a red precipitate of $[Fe(CO)_2(thf)(\eta\text{-}C_5H_5)][PF_6]$ (**9**) (90 mg, 40%) m.p. > 130 °C (dec.) [Lit. [9] 103 °C (dec.)] (Found: C, 32.34; H, 3.18; $C_{11}H_{13}F_6FeO_3P$ calc: C, 33.53; H, 3.33%). Infrared (Nujol): ν(CO) 2072s, 2025s; ν(PF) 890vs(br), 840vs(br) cm^{-1}; other bands at 1428s, 1028s cm^{-1}. ν(CO) (CH_2Cl_2) 2068s, 2025s cm^{-1} [Lit. [9] (CH_2Cl_2) 2065, 2019 cm^{-1}]. ^{1}H NMR: δ (CD_2Cl_2) 1.83 (m, 4H, CH_2), 3.45 (m, 4H, OCH_2), 5.38 (s, 5H, C_5H_5) [Lit. [9] δ (acetone-d_6) 1.82 (m, 4H, CH_2), 3.63 (m, 4H, OCH_2), 5.71 (s, 5H, C_5H_5)]. Recrystallisation (acetone/EtOH) over 14 days (−30 °C) gave yellow crystals of $[Fe(CO)_3(\eta\text{-}C_5H_5)][PF_6]$ (**10**) (11 mg, 5%) m.p. > 250 °C (dec.) [Lit. [14] 250–255 °C (dec.)] (Found: C, 27.10; H, 1.48; *M* (cation) 205; $C_8H_5F_6FeO_3P$ calc: C, 27.46; H, 1.44%; *M* (FAB/MS) *m/z* 205). Infrared (Nujol): ν(CO) 2127s, 2070s cm^{-1} [Lit. [10] 2127, 2070 cm^{-1}], ν(PF) 840vs(br).

FAB mass spectra

The matrix was 3-nitrobenzyl alcohol or dithioerythritol/dithiothreitol (1/6); complexes were dissolved in acetone or dichloromethane (ca. 0.5 *M*) and a drop of a solution was added to a drop of the matrix. The resulting mixture was then applied to the tip of the FAB probe. The following spectra were obtained (*m/z*, based on ^{56}Fe or ^{102}Ru, assignment, relative intensity). Peaks marked ★ are the centres of overlapping multiplets consisting of the assigned ion, and ions related to it by loss of one or two H atoms.

(i) [Fe{C=CPh(C$_7$H$_7$)}(dppe)(η-C$_5$H$_5$)][PF$_6$] (8). 711, $[M]^+$, 5; 634, $[M - Ph]^+$, 3; 620, $[M - C_7H_7]^+$, 100; 555, $[M - C_7H_7 - C_5H_5]$, 5; 519, $[Fe(dppe)(C_5H_5)]^+$, 80; 497, –, 4; 472, –, 4; 454, $[519 - C_5H_5]^+$, 12; 442, $[519 - C_6H_5]^+$, 8; 426, $[Fe(PPh_2)_2]^+$, 50; 398, $[dppe]^+$, 7; 390, –, 13; 332, $[Fe(C_2H_2PPh_2)(C_5H_5)]^+$, 9; 320, $[Fe(CH_2PPh_2)(C_5H_5)]^+$, 15; 306, $[Fe(PPh_2)(C_5H_5)]^+$, 47.

(ii) [Ru{C=CPh(C$_7$H$_7$)}(dppe)(η-C$_5$H$_5$)][PF$_6$] (3). 911, $[M + matrix]^-$, 1; 757, $[M]^+$, 7; 680, $[M - Ph]^+$, 5; 666, $[M - C_7H_7]^+$, 50; 565, $[Ru(dppe)(C_5H_5)]^+$, 100; 379★, $[Ru(C_2H_4PPh_2)(C_5H_5)]^+$, 33; 350★, $[Ru(PPh_2)(C_5H_5)]^+$, 61.

(iii) [Ru{C=C(C$_6$F$_5$)(C$_7$H$_7$)}(PPh$_3$)$_2$(η-C$_5$H$_5$)][PF$_6$] (4). 989, ?$[M + O]^+$, 2; 973, $[M]^+$, 42; 954, $[M - F]^+$, 4; 898★, ?$[882 + O]^+$, 2; 882 $[M - C_7H_7]^+$, 62; 863★, $[M - F - C_7H_7]^+$, 6; 711★, $[M - PPh_3]^+$, 10; 691, $[Ru(PPh_3)_2(\eta\text{-}C_5H_5)]^+$, 9; 646★, –, 5; 633★, –, 8; 619★, $[Ru(C_2C_6F_5)(PPh_3)(C_5H_5)]^+$, 17; 542, $[619 - Ph]^+$, 44; 448★, $[RuF(PPh_3)(C_5H_5)]^+$, 17; 429★, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 363★, –, 12; 352★, $[Ru(PPh_2)(C_5H_5)]^+$, 24; 287, $[Ru(PPh_2)]^+$, 14; 244, $[RuPh(C_5H_5)]^+$, 28; 167, $[Ru(C_5H_5)]^+$, 14.

(iv) [Fe(CO)$_2$(thf)(η-C$_5$H$_5$)][PF$_6$] (9). 274, –, 35; 249, $[M]^+$, 100; 221, $[M - CO]^+$, 26; 193, $[M - 2CO]$, 74; 177, $[M - thf]^+$, 10; several other peaks < 5% were observed up to *m/z* 622.

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