*Journal of Organometallic Chemistry*, 299 (1986) C51—C55
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

**Preliminary communication**

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# STEREO- AND REGIO-SPECIFIC C—C BOND FORMATION VIA THE COUPLING OF ELECTROPHILIC AND NUCLEOPHILIC ORGANOTRANSITION-METAL COMPLEXES: THE X-RAY CRYSTAL STRUCTURE OF $[Ru(CO)_2(PPh_3)(\eta^2,\eta^3\text{-}C_8H_8R)][PF_6]\cdot 0.5CH_2Cl_2$ $(R = CH_2C(Me)=CH_2)$

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(Received October 15th, 1985)

## Summary

The coupling of $[Ru(CO)_2L(\eta^4\text{-cot})]$ (L = CO or $PPh_3$, cot = cyclooctatetraene) with $[Fe(CO)_3(\eta^5\text{-cyclohexadienyl})]^+$ or $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})]^+$ yields respectively the dimetallic species $[Ru(CO)_2L(\eta^2,\eta^3\text{-}C_8H_8\{Fe(CO)_3(\eta^4\text{-}C_6H_7)\}]$ (**3**) and the allyl-substituted derivative $[Ru(CO)_2L(\eta^5\text{-}C_8H_8CH_2C(Me)=CH_2)][PF_6]$ (**5**) whose X-ray structure is reported; paramagnetic $[Co(\eta\text{-}C_5H_5)_2]$ and $[Ru(CO)_3(\eta^5\text{-cyclohexadienyl})]^+$ give diamagnetic $[Ru(CO)_3(\eta^4\text{-}C_6H_7C_5H_6(\sigma\text{-}C_5H_5)]$ (**8**) via C—C bond formation and one-electron reduction.

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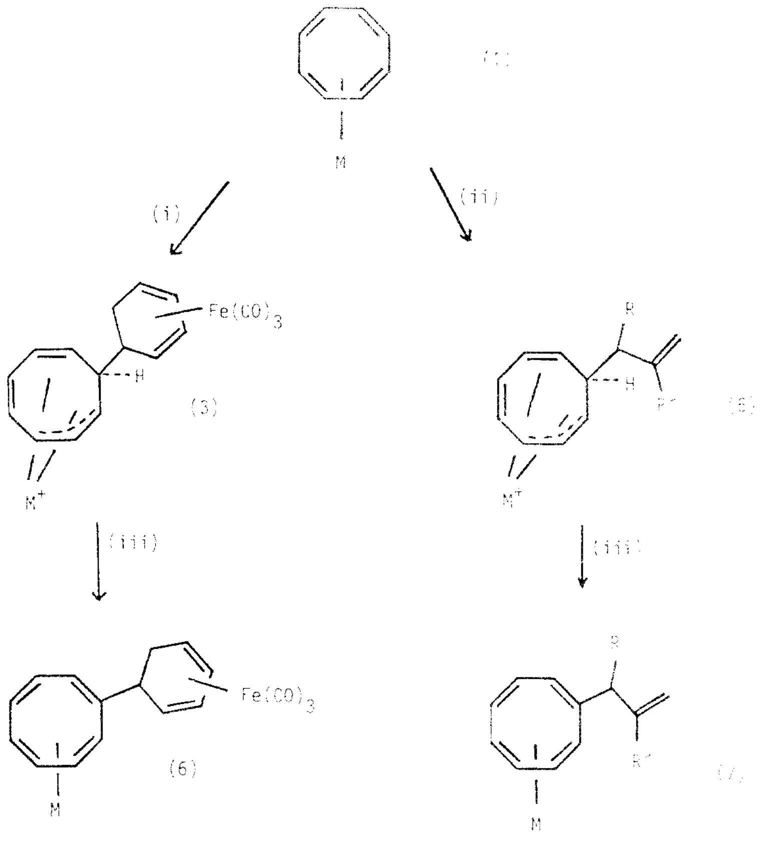
The synthesis of carbon—carbon bonds in organometallic chemistry routinely involves the addition of a carbon-based nucleophile to a coordinated hydrocarbon [1]. Reactions involving the electrophilic addition of a carbocation are, however, far less common [2], due in part to the relative scarcity of suitable, easily handled, reagents.

We now show that stereo- and regio-selective C—C bond formation can be readily effected by the addition of an organometallic electrophile, functioning as a stable source of a reactive carbocation, to an electron-rich (and therefore nucleophilic) transition metal $\pi$-complex. The generality of this method is illustrated here by the use of cationic allyl and cyclohexadienyl complexes as carbocation sources. As far as we are aware, the only previous examples of this approach involved the reactions of $[Fe(\sigma\text{-allyl})(CO)_2(\eta\text{-}C_5H_5)]$ with $[Fe(CO)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)]^+$ and $[Fe(CO)_3(\eta^5\text{-cycloheptatrienyl})]^+$ [3].

0022-328X/86/$03.50

At room temperature in $CH_2Cl_2$, $[Ru(CO)_2L(\eta^4\text{-cot})]$ (1; L = CO or $PPh_3$, cot = cyclooctatetraene) and $[M(CO)_3(\eta^5\text{-}C_6H_7)][BF_4]$ (2, M = Fe, $C_6H_7$ = cyclohexadienyl) gave a pale yellow solution from which the white product $[Ru(CO)_2L(\eta^2,\eta^3\text{-}C_8H_8R)][BF_4]$ (3; e.g. R = $Fe(CO)_3(\eta^4\text{-}C_6H_7)$, L = CO, 75%, $\tilde{\nu}$(CO) ($CH_2Cl_2$) 2 131, 2 087, 2 068, 2 050, and 1 978 $cm^{-1}$) was isolated on adding diethyl ether. The structure of 3 (Scheme 1), was identified by $^1H$ and $^{13}C$ NMR spectroscopy*; the eight-membered ring, $\eta^2,\eta^3$-bonded to ruthenium, and the substituted cyclohexadiene group, $\eta^4$-bound to iron, are coupled at the terminal carbon atom of the dienyl ligand in 2.

A similar reaction between 1 (M = Ru) and $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})][PF_6]$ (4; allyl = $C_3H_5$, $C_3H_4Me$-1, or $C_3H_4Me$-2) [4] resulted in a deep red solution from which white $[Ru(CO)_2L(\eta^5\text{-}C_8H_8R)][PF_6]$ (5; e.g. L = CO, R = $CH_2CH{:}CH_2$, 58%, $\tilde{\nu}$(CO) ($CH_2Cl_2$) 2 130, 2 081, and 2071 $cm^{-1}$) and orange $[Fe\{P(OMe)_3\}_2(NO)_2]$ ($\tilde{\nu}$(NO)(n-hexane) 1744 and 1693 $cm^{-1}$) were separated. Electrophilic allylation of the $C_8$-ring, via the terminal carbon atom of the $C_3$-fragment, and loss of the $Fe\{P(OMe)_3\}$-



SCHEME 1: M = $Ru(CO)_2L$, L = CO or $PPh_3$; R, R' = H, Me. (i) $[Fe(CO)_3(\eta^5\text{-}C_6H_7)]^+$ (2, M = Fe). (ii) $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})]^+$(4), (iii) $NEt_3$.

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*Details of the spectra are omitted for the sake of brevity.

$(NO)_2$ group from the initial adduct between 1 and 4, were verified by an X-ray crystallographic study on 5 (L = $PPh_3$, R = $CH_2C(Me)=CH_2$).

*Crystal data:* Complex 5 (L = $PPh_3$, R = $CH_2C(Me)=CH_2$) as its hemi-dichloromethane solvate: $C_{32}H_{30}F_6P_2Ru \cdot 0.5CH_2Cl_2$, $M$ = 765.5, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, No. 14), $a$ 12.984(8), $b$ 11.602(2), $c$ 21.99(1) Å, $\beta$ 96.57(5)°, $U$ 3 291(3) Å$^3$, room temp., $Z$ = 4, $D_c$ 1.55 g cm$^{-3}$, $F(000)$ 1548 electrons, graphite-monochromated X-radiation, $\bar{\lambda}$ = 0.71069 Å, $\mu$(Mo-$K_\alpha$) 7.05 cm$^{-1}$. Data were collected for a unique quadrant of reciprocal space in the range $4 < 2\theta < 50°$ on a Nicolet P3m diffractometer. The structure was solved by the heavy atom method and refined by least squares to give a residual index $R$ of 0.052 for 3686 unique, absorption-corrected, observed $[I > 2\sigma(I)]$, intensity data. The anion and solvent are both disordered, the latter about a crystallographic inversion centre. The $C_8$-ring hydrogen atoms were located and refined freely.

The geometry of the cation of 5 (L = $PPh_3$, R = $CH_2CH(Me)=CH_2$) is shown in Fig. 1. The ruthenium atom is bonded to the $C_8$-ring, in the $\eta^2,\eta^3$-mode found for 3 and for $[Ru(\eta^5\text{-}C_8H_9)(\eta^6\text{-mesitylene})]^+$ [5], to two carbonyls, and to $PPh_3$ which is *trans* to the $\eta^2$-alkene bond C(6)—C(7); the allyl group C(9)—C(10)—C(11) is stereospecifically joined to the $C_8$-ring as an *exo*-substituent, via bond C(8)—C(9).

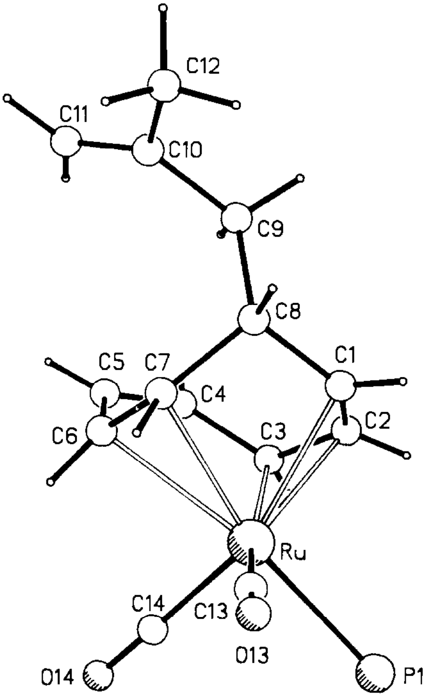
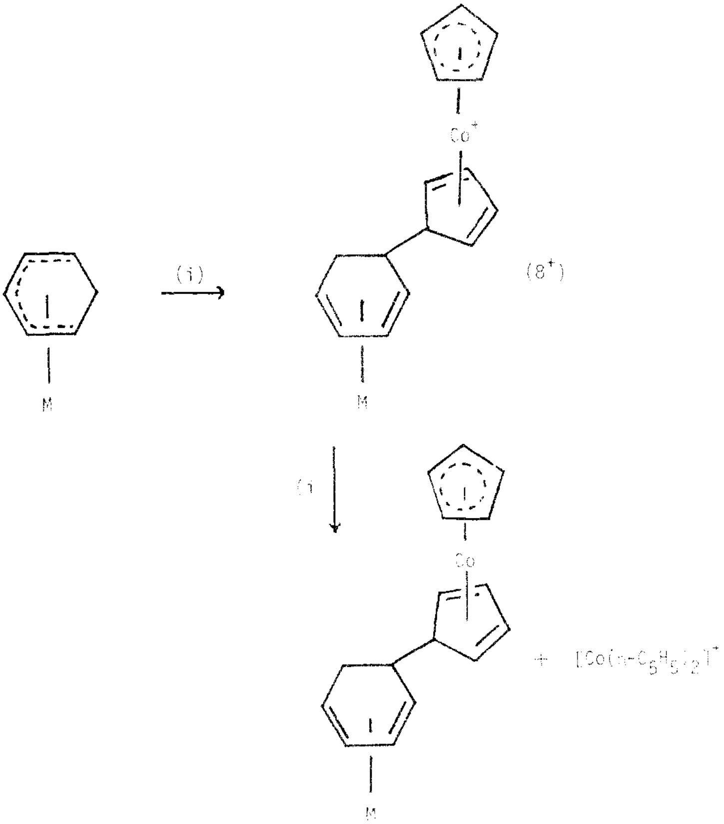


Fig. 1. The geometry of the cation of 5 (L = $PPh_3$, R = $CH_2C(Me)=CH_2$] the phenyl groups have been omitted for clarity. Important interatomic distances are Ru—C(1) 2.336(6), Ru—C(2) 2.210(6), Ru—C(3) 2.232(6), Ru—C(6) 2.420(7), Ru—C(7) 2.393(7), C(1)—C(8) 1.499(10), C(1)—C(2) 1.367(9), C(2)—C(3) 1.413(9), C(3)—C(4) 1.463(10), C(4)—C(5) 1.306(11), C(5)—C(6) 1.448(10), C(6)—C(7) 1.356(9), C(7)—C(8) 1.501(9), C(8)—C(9) 1.508(10), C(9)—C(10) 1.494(12), C(10)—C(11) 1.283(14) Å.

Two other aspects of the reaction between 1 and 4 are noteworthy. First, it is regiospecific in that the new C—C bond in 5 (L = PPh$_3$, R = CH(Me)CH=CH$_2$) is almost exclusively (at least 85%, by $^1$H NMR spectroscopy) formed by the coupling of the CHMe terminus of the allyl group of 4 (allyl = C$_3$H$_4$Me-1) with the C$_8$-ring. Second, diastereoisomerism is observed for 5 (R = CH(Me)CH=CH$_2$); the two chiral centres are at C(8) (Fig. 1), found in all examples of 5, and at C(9).

Both 3 and 5 are readily deprotonated by NEt$_3$ in CH$_2$Cl$_2$, giving the red, crystalline, cot derivatives 6 (M = Ru, L = PPh$_3$; 59%; $\tilde{\nu}$(CO)(n-hexane) 2049, 2003, 1978, and 1947 cm$^{-1}$) and 7 (M = Ru, L = PPh$_3$; 28%; $\tilde{\nu}$(CO)(n-hexane) 2002 and 1946 cm$^{-1}$), respectively (Scheme 1). Thus, the overall electrophilic substitution of the coordinated C$_8$ ring of 1 is rapidly and simply achieved in overall yields of 15—40%.

The coupling reactions described are not confined to electron-rich cot complexes. For example 2 (M = Ru) and paramagnetic [Co($\eta$-C$_5$H$_5$)$_2$] (in a 1/2 ratio) in toluene give [Co($\eta^4$-C$_5$H$_5$R)($\eta$-C$_5$H$_5$)] as deep red, diamagnetic crystals (8; R = Ru(CO)$_3$($\eta^4$-C$_6$H$_7$), 10%, $\tilde{\nu}$(CO)(n-hexane) 2059, 1994, and 1987 cm$^{-1}$; *m/e* = 454] (Scheme 2). The formation of 8 differs from those of 3 and 5 in that a one-electron reduction process is also required. Complex



SCHEME 2. M = Ru(CO)$_3$ (2, M = Ru). (i) [Co($\eta$-C$_5$H$_5$)$_2$].

8 undergoes one-electron oxidation* at ca. 0.1 V (vs. the saturated calomel electrode) so that the reduction of $8^+$, the initial adduct formed between 2 (M = Ru) and $[Co(\eta\text{-}C_5H_5)_2]$, would certainly occur with a second equivalent of cobaltocene (the oxidation of which, to $[Co(\eta\text{-}C_5H_5)_2]^+$, occurs at —0.9 V) (Scheme 2).

**Acknowledgements.** We thank the S.E.R.C. for a Research Studentship (to J.B.S.) and Johnson Matthey for a generous loan of ruthenium trichloride.

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*This process is irreversible in $CH_2Cl_2$, but this does not rule out the mechanism shown in Scheme 2 which refers to the reaction in toluene at 0°C.