Reaction of [Rh(η^4-cot)(η-C_5H_5)] (cot = Cyclo-octatetraene) with [Fe{P(OMe)$_3$}(NO)$_2$(η^3-CH_2CHCH_2)]$^+$: Allylic Alkylation of a Cyclopentadienyl Ring

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The reaction of [Rh(η^4-cot)(η-C_5H_5)] (cot = cyclo-octatetraene) with [Fe{P(OMe)$_3$}(NO)$_2$(η^3-CH_2CHCH_2)][PF_6] gives [Rh(η^2,η^3-C_8H_9)(η-C_5H_4R)][PF_6] (R = $CH_2CH{=}CH_2$) *via* allyl addition to the cyclopentadienyl ring and proton migration to the co-ordinated cot.

We have recently described the allylic alkylation reactions of [M(CO)$_2$L(η^4-cot)] (M = Fe, L = CNBu^t;[1] M = Ru, L = CO or PPh$_3$; cot = cyclo-octatetraene)[1,2] and [Co(η^4-cot)(η-C_5R_5)][3] (R = H or Me) with [Fe{P(OMe)$_3$}(NO)$_2$(η^3-allyl)][PF_6] (**1**), all of which involve allyl transfer from the dinitrosyl iron complex to the co-ordinated cot ligand. In the cases of iron and ruthenium, deprotonation of the initially formed adducts followed by ligand detachment provides a route to allyl-substituted cyclo-octatetraenes;[1] for cobalt, the initial adducts undergo C_8-ring rearrangements to give the tetrahydropentalenyl derivatives [Co(η^5-L)(η-C_5R_5)]$^+$ (L = $C_8H_8CH_2CH{=}CH_2$; R = H or Me) (Figure). We now show that the reaction of complex (**1**) with [Rh(η^4-cot)(η-C_5H_5)] differs from those with the cot complexes of Fe, Ru, and Co in giving the allyl-substituted cyclopentadienyl derivative [Rh(η^2,η^3-C_8H_9)(η-C_5H_4R)][PF_6] (**2**; R = $CH_2CH{=}CH_2$).

Results and Discussion

Treatment of [Rh(η^4-cot)(η-C_5H_5)] with [Fe{P(OMe)$_3$}(NO)$_2$(η^3-CH_2CHCH_2)][PF_6] (**1**) in CH_2Cl_2 gave a brown solution from which an orange solid was isolated after purification from CH_2Cl_2–diethyl ether; the neutral compound [Fe{P(OMe)$_3$}$_2$(NO)$_2$] was formed as a by-product. The orange solid was chacterised as [Rh(η^2,η^3-C_8H_9)(η-C_5H_4R)][PF_6] (**2**; R = $CH_2CH{=}CH_2$) (Scheme) by elemental analysis and by ^1H and ^{13}C n.m.r. spectroscopy (Table). The 400-MHz ^1H n.m.r. spectrum clearly reveals that allylic substitution of the cyclopentadienyl ring has occurred rather than addition to the cot ligand. First, the signals for the cyclopentadienyl protons appear as a complex multiplet centred at δ 5.70; a doublet is expected for an η^5-C_5H_5 group bonded to rhodium (^{103}Rh, $I = \frac{1}{2}$). Secondly the methylene protons, H^{14} and $H^{14'}$, of the allyl group show coupling only to H^{15}. The ^1H n.m.r. spectrum also shows that the cot ring has undergone proton addition to give an η^2,η^3-cyclo-octatrienyl ligand. The chemical shifts of the C_8-ring protons of (**2**) and of [Rh(η^2,η^3-C_8H_9)(η^5-L)]$^+$ (L = cyclopentadienyl[4] or indenyl[5]) are very similar; five of these protons of (**2**), namely H^1—H^3, H^6 and H^7, show coupling (*ca.* 2 Hz) to the rhodium atom.

The ^{13}C n.m.r. spectrum of complex (**2**) shows that the shifts of the C_8-ring signals are also in close agreement with those of the C_8H_9 carbon atoms of [Rh(η^2,η^3-C_8H_9)(η-C_5H_5)]$^+$;[4] due to the asymmetry of the cyclo-octatrienyl ligand, five signals are observed for the cyclopentadienyl ring carbons. All ten of the metal-co-ordinated carbon atoms show signals with rhodium coupling of 4—11 Hz.

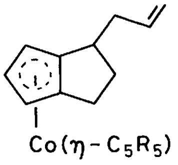
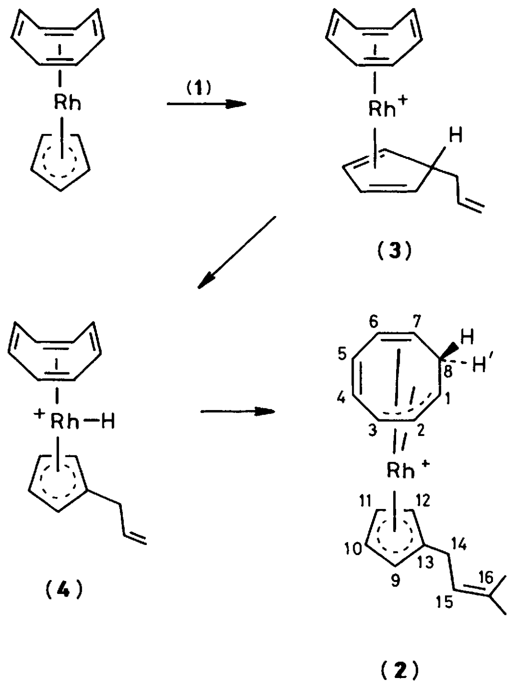


Figure. R = H or Me



Scheme.

There are precedents for the preferential attack of an electrophile at an η-C_5H_5 group rather than a co-ordinated diene in [Rh(η^4-diene)(η-C_5H_5)]. For example, the 1,3-cyclohexadiene (chd) complex [Rh(η^4-chd)(η-C_5H_5)] undergoes Friedel–Crafts acylation to give [Rh(η^4-chd){η^5-C_5H_4(COMe)}],[6] and [Rh(η^4-cod)(η-C_5H_5)] (cod = cyclo-octa-1,5-diene) reacts with [CPh_3][BF_4] to give [Rh(η^4-cod){η^5-C_5H_4(CPh_3)}].[7]

Table. Room-temperature ^{1}H and ^{13}C n.m.r. data for $[Rh(\eta^{2},\eta^{3}\text{-}C_{8}H_{9})(\eta^{5}\text{-}C_{5}H_{4}R)]^{+}$ (**2**; R = $CH_{2}CH{=}CH_{2}$) in $CD_{2}Cl_{2}$

$^{1}H^{b}$ (δ)

2.96 [1 H, m, $J(H^{8}H^{8'})$ 12.9, $J(H^{8}H^{1})$ = $J(H^{8}H^{7})$ 6.5, H^{8}], 3.11 [2 H, d, $J(H^{14}H^{15})$ = $J(H^{14'}H^{15})$ 6.8, H^{14}, $H^{14'}$], 3.39 [1 H, ddd $J(H^{8'}H^{8})$ 13.1, $J(H^{8'}H^{1})$ 9.4, $J(H^{8'}H^{7})$ 7.4, $H^{8'}$], 3.95 [1 H, dq, $J(H^{7}H^{6})$ = $J(H^{7}H^{8})$ = $J(H^{7}H^{8'})$ 7.3, $J(H^{7}Rh)$ 1.7, H^{7}], 4.57 [1 H, dt, $J(H^{2}H^{1})$ = $J(H^{2}H^{3})$ 7.8, $J(H^{2}Rh)$ 1.7, H^{2}], 4.95 [1 H, m, $J(H^{1}H^{8'})$ 9.5, $J(H^{1}H^{2})$ = $J(H^{1}H^{8})$ 7.1, H^{1}], 5.21 [2 H, m, $J(H^{16}H^{15})$ 17.3, $J(H^{16'}H^{15})$ 10.0, H^{16}, $H^{16'}$], 5.40 [1 H, dd, $J(H^{4}H^{5})$ 7.1, $J(H^{4}H^{3})$, 3.7, H^{4}], 5.49 (2 H, m, H^{3}, H^{5}), 5.57 [1 H, dt, $J(H^{6}H^{7})$ 7.6, H^{6}], 5.70 (4 H, m, H^{9}, H^{10}, H^{11}, H^{12}), 5.90 [1 H, ddt, $J(H^{15}H^{16})$ 17.3, $J(H^{15}H^{16'})$ 9.8, $J(H^{15}H^{14})$ = $J(H^{15}H^{14'})$ 6.8, H^{15}]

$^{13}C^{c}$ (δ/p.p.m.)

19.67 (C^{8}), 31.57 (C^{14}), 41.08 [d, $J(C^{7}Rh)$ 6.1, C^{7}], 47.55 [d, $J(C^{1}Rh)$ 4.6, C^{1}], 79.93 [d, $J(C^{3}Rh)$ 10.7, C^{3}], 84.97 [d, $J(C^{2}Rh)$ 6.1, C^{2}],89.38 [d, $J(CRh)$ 4.6], 89.44 [d, $J(CRh)$ 4.5], 89.61 [d, $J(CRh)$ 4.6], 90.16 [d, $J(CRh)$ 6.1, C^{9}, C^{10}, C^{11}, C^{12}], 91.96 [d, $J(C^{6}Rh)$ 10.7, C^{6}], 112.85 [d, $J(C^{13}Rh)$ 4.5, C^{13}], 119.00 (C^{16}), 131.03, 132.35 (C^{5}, C^{6}), 133.41 (C^{15})

[a] Atom numbering is shown in the Scheme (*J* values in Hz). [b] 400-MHz Spectrum. [c] 100.5-MHz Spectrum.

The second example contrasts with the reaction between $[CPh_{3}]^{+}$ and $[Co(\eta^{4}\text{-cod})(\eta\text{-}C_{5}H_{5})]$ where hydride abstraction from the cyclo-octadiene is observed.[7] It is notable that both complexes $[Rh(\eta^{4}\text{-diene})(\eta\text{-}C_{5}H_{5})]$ (diene = chd or cod) undergo protonation at the diene, probably *via* initial attack at the metal.[6,8] Thus, the site of attack on $[Rh(\eta^{4}\text{-diene})(\eta\text{-}C_{5}H_{5})]$ seems to depend on the electrophile.

The mechanism proposed for the formation of (**2**) is shown in the Scheme and involves initial electrophilic addition of complex (**1**) to the cyclopentadienyl ring of $[Rh(\eta^{4}\text{-cot})(\eta\text{-}C_{5}H_{5})]$ giving the 16-electron cyclopentadiene complex $[Rh(\eta^{4}\text{-cot})(\eta^{4}\text{-}C_{5}H_{5}R)]^{+}$ (**3**; R = $CH_{2}CH{=}CH_{2}$) [after loss of the $Fe\{P(OMe)_{3}\}(NO)_{2}$ fragment]. Allylic addition to the $C_{5}H_{5}$ ring is assumed to occur *exo* to the rhodium atom by analogy with the formation of $[Ru(CO)_{2}(PPh_{3})(\eta^{2},\eta^{3}\text{-}C_{8}H_{8}R)]^{+}$ (R = $CH_{2}CH{=}CH_{2}$), from complex (**1**) and $[Ru(CO)_{2}(PPh_{3})(\eta^{4}\text{-cot})]$,[1,2] where the geometry of the adduct was confirmed by *X*-ray crystallography. The *endo* proton of the $C_{5}H_{5}R$ ligand of (**3**) then migrates to take up the *endo* position of the CH_{2} group in the $C_{8}H_{9}$ ring of the 18-electron complex (**2**), most probably *via* the metal hydride (**4**). The metal-to-ring migration step, which converts (**4**) into (**2**), is similar to that proposed to account for the formation of $[Rh(\eta^{2},\eta^{3}\text{-}C_{8}H_{8}D)(\eta\text{-}C_{5}H_{5})]^{+}$, from $[Rh(\eta^{4}\text{-cot})(\eta\text{-}C_{5}H_{5})]$ and $CF_{3}CO_{2}D$,[4] where the deuterium occupies the *endo* position.

Metal hydride intermediates analogous to complex (**4**) may also be formed in the reactions noted above of $[Rh(\eta^{4}\text{-diene})(\eta\text{-}C_{5}H_{5})]$ (diene = chd or cod) with carbon-based nucleophiles.[6,7] In these cases, however, proton migration to the diene cannot result in the formation of a stable, 18-electron η^{5}-dienyl complex; neither chd nor cod has the necessary unco-ordinated alkenic bond at which protonation can occur [*cf.* the cot ligand in complex (**4**) (Scheme)]. Thus, proton loss from the metal gives the neutral compounds $[Rh(\eta^{4}\text{-diene})(\eta^{5}\text{-}C_{5}H_{4}R)]$ (R = COMe or CPh_{3}).

In order to shed further light on the allylic alkylation reaction of $[Rh(\eta^{4}\text{-cot})(\eta\text{-}C_{5}H_{5})]$, complex (**1**) was treated with $[Rh(\eta^{4}\text{-cot})(\eta\text{-}C_{5}Me_{5})]$ (where electrophilic addition to the C_{5} ring would seem to be ruled out). An orange product was isolated but the ^{1}H n.m.r. spectrum revealed the presence of three inseparable products and no further characterisation was possible.

Experimental

The preparation and purification of the complex described was carried out under an atmosphere of dry nitrogen. The complexes $[Rh(\eta^{4}\text{-cot})(\eta\text{-}C_{5}H_{5})]$[9] and $[Fe\{P(OMe)_{3}\}(NO)_{2}(\eta^{3}\text{-}CH_{2}CHCH_{2})][PF_{6}]$[10] were prepared by published methods.

N.m.r. spectra were recorded on a JEOL GX400 spectrometer and calibrated against $SiMe_{4}$ as an internal reference. Microanalysis was by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Allylcyclopentadienyl(1—3-η,6—7-η-cyclo-octa-2,4,6-trien-1-yl)rhodium Hexafluorophosphate, $[Rh(\eta^{2},\eta^{3}\text{-}C_{8}H_{9})(\eta^{5}\text{-}C_{5}H_{4}R)][PF_{6}]$ (R = $CH_{2}CH{=}CH_{2}$).—To a stirred solution of $[Rh(\eta^{4}\text{-cot})(\eta\text{-}C_{5}H_{5})]$ (0.09 g, 0.31 mmol) in $CH_{2}Cl_{2}$ (20 cm^{3}) was added $[Fe\{P(OMe)_{3}\}(NO)_{2}(\eta^{3}\text{-}CH_{2}CHCH_{2})][PF_{6}]$ (0.13 g, 0.31 mmol). After 30 min the dark brown solution was filtered and evaporated to dryness. The residue was dissolved in $CH_{2}Cl_{2}$. This solution was filtered and treated with diethyl ether to precipitate the product. Repetition of this procedure gave an orange solid, yield 0.09 g (63%) (Found: C, 41.7; H, 4.1. $C_{16}H_{18}F_{6}PRh$ requires C, 41.9; H, 4.0%).

The complex dissolves in polar solvents such as $CH_{2}Cl_{2}$ to give orange solutions which slowly decompose in air.

Acknowledgements

We thank the S.E.R.C. for a Studentship (to M. G.) and Johnson Matthey for a generous loan of rhodium trichloride.

References

1. N. G. Connelly, M. Gilbert, A. G. Orpen, and J. B. Sheridan, *J. Chem. Soc., Dalton Trans.*, in the press.
2. N. G. Connelly, A. G. Orpen, I. C. Quarmby, and J. B. Sheridan, *J. Organomet. Chem.*, 1986, **299**, C51.
3. N. G. Connelly, M. Gilbert, A. G. Orpen, and J. M. White, *J. Chem. Soc., Dalton Trans.*, 1988, 1631.
4. J. Evans, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J. Chem. Soc., Dalton Trans.*, 1974, 2375.
5. D. T. Clark, M. Mlekuz, B. G. Sayer, B. E. McCarry, and M. J. McGlinchey, *Organometallics*, 1987, **6**, 2201.
6. B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J. Chem. Soc., Dalton Trans.*, 1972, 2084.
7. J. Lewis and A. W. Parkins, *J. Chem. Soc. A*, 1967, 1150.
8. J. Evans, B. F. G. Johnson, and J. Lewis, *Chem. Commun.*, 1971, 1252.
9. L. Brammer, N. G. Connelly, J. Edwin, W. E. Geiger, A. G. Orpen, and J. B. Sheridan, *Organometallics*, 1988, **7**, 1259.
10. P. K. Baker, S. Clamp, N. G. Connelly, M. Murray, and J. B. Sheridan, *J. Chem. Soc., Dalton Trans.*, 1986, 459.

Received 4th *May* 1989; *Paper* 9/01879D