

The Parallel between Phenyl-initiated C–C Coupling Reactions in Dirhodium Complexes and those Catalysed by Rhodium Particles

Zhi-Qiang Wang, Helen C. Long, Michael L. Turner and Peter M. Maitlis*

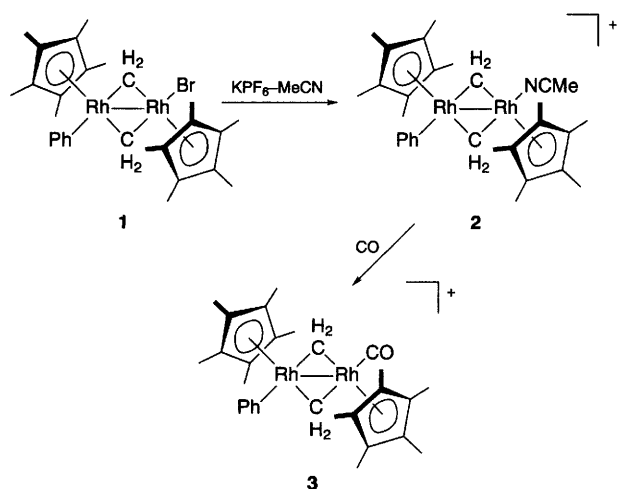
Department of Chemistry, The University, Sheffield, UK S3 7HF

Decomposition of $[(C_5Me_5)Rh(\mu-CH_2)_2(Ph)(CO)]^+$ (homogeneously, under CO) in solution gives $PhCH=CH_2$, $PhMe$ and C_6H_6 , while phenyl (from Ph) reacts with surface methylene (from CO + H_2) heterogeneously over rhodium metal to give $PhEt$, $PhMe$ and C_6H_6 ; it is proposed that the two reactions are also related mechanistically.

We are investigating metal-promoted C–C coupling processes to see how far those that occur homogeneously in solution¹ can be mimicked heterogeneously on metal surfaces.²

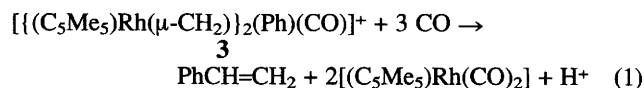
The reactions of model dinuclear rhodium complexes, and heterogeneous labelling studies over rhodium catalysts, have shown that a key path for the CH_2 polymerisations which take place during the hydrogenation of CO in Fischer–Tropsch reactions, is between surface *alkenyls* and surface methylenes.¹ This is in preference to the previously proposed reaction between surface *alkyls* and methylenes.³ We now highlight a general concept that, where alternative pathways can exist, the coupling of a metal-bonded sp^2 carbon to a metal-bonded sp^3 (or another sp^2) carbon is preferred to the coupling between two metal-bonded alkyl sp^3 carbons.⁴ This can be understood because the latter is a direct reductive elimination, while the former can occur as a *migration* process (followed by decomplexation) with a lower activation energy. Calhorda *et al.* have provided theoretical explanations for such concepts in coupling reactions on palladium and nickel complexes in solution.⁵ Our thesis, that this can occur both in solution and on a surface, is further illustrated by an analysis of C–C and C–C–C coupling reactions initiated by phenyl species, both in dirhodium complexes and over heterogeneous catalysts.

The *trans*-phenyl-bromo di- μ -methylene dirhodium complex **1**,⁶ reacted with KPF_6 in acetonitrile to yield the cationic acetonitrile complex $[(C_5Me_5)Rh(\mu-CH_2)_2(Ph)(MeCN)]PF_6$ **2**.[†] The acetonitrile was readily displaced by carbon monoxide (1 atm, 0 °C, 10 min) in CH_2Cl_2 or acetone solution to give the unstable cationic carbonyl $[(C_5Me_5)Rh(\mu-CH_2)_2(Ph)(CO)]PF_6$ **3** (Scheme 1). This single isomer, showing one $\nu(CO)$ band at 2070 cm^{-1} , was assigned the *trans* geometry on the basis of its 1H NMR spectrum.^{6,7‡} On standing in solution in the absence of added acid at +25 °C, **3** decomposed to give $[(C_5Me_5)Rh(CO)_2]$ as the chief organometallic species [$\nu(CO)$ 1950, 2018 cm^{-1}]. GC and GC–MS analysis showed that the organic products from decomposition of complex **3** (10 μ mol; acetone solution, 25 °C, 6 h) were



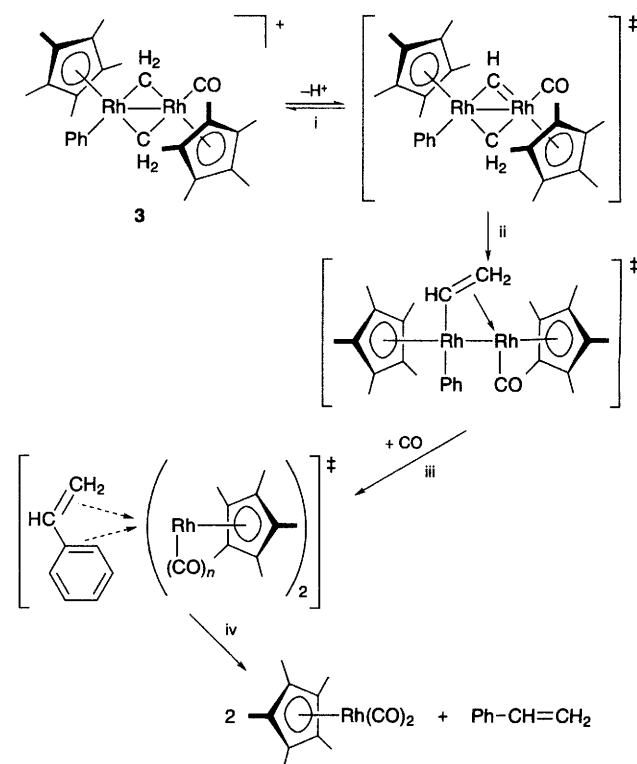
Scheme 1 The synthesis of complex **3**

composed of benzene (0.4 μ mol), toluene (0.4 μ mol), and styrene (6.0 μ mol), together with some of the ketone, $PhCH_2COMe$ (1.2 μ mol), giving a materials balance of 80%. The reaction leading to the major organic product, styrene, proceeds according to equation (1)



Monitoring the rate of disappearance of the $\nu(CO)$ at 2070 cm^{-1} (CH_2Cl_2 solution, 25 °C) showed that in the absence of added acid, *trans*-**3** decomposed in a first-order rate process ($k_{obs} = 4.7 \pm 0.1 \times 10^{-3} s^{-1}$).[§] Styrene formation was however inhibited on addition of 10 equivalents of acid. We propose that styrene formation proceeds stepwise (Scheme 2). Step (i) is a (reversible) loss of H^+ from **3**, generating a μ -methyne ($\mu-CH$) intermediate onto which the μ -methylene ($\mu-CH_2$) then migrates in step (ii) to give a vinyl ($-CH=CH_2$), which in turn migrates [step (iii)] onto the $Ph-Rh$ ($sp^2 + sp^2$) to give styrene via an η -styrene intermediate [step (iv)]. Toluene can arise by a phenyl + methylene coupling followed by protonation of the resulting benzyl. Rhodium catalysts have been previously reported to give styrene from reaction of benzene and ethylene.⁸

Since carbon monoxide and hydrogen are known to yield CH_2 species as initial products on metal surfaces,² we also



Scheme 2 Proposed mechanism for the formation of styrene from the decomposition of complex **3** (see text)

carried out reactions in which iodobenzene (giving phenyl) and CO + H₂ (giving CH₂) were reacted together over a heterogeneous rhodium catalyst. After the attainment of steady-state conditions [rhodium (4%)–ceria (9%)–silica catalyst;^{1,9} 2.5 h on stream, 1 atm, 225 °C, CO–H₂ (1 : 2); flow rate 0.5 l h⁻¹], pulses of iodobenzene (1 μl, 130 μmol g⁻¹ h⁻¹) were added to the stream. Analysis of the products showed no significant change in either activity or selectivity of the Fischer–Tropsch reaction on addition of the iodobenzene and the chain growth probability, α , remained constant at 0.58 for alkene/alkane formation.

GC and GC-MS analysis of the products showed the presence of the aromatics, benzene, toluene, ethylbenzene, *n*-propylbenzene and *n*-butylbenzene (ratio 44 : 50 : 1 : 0.1 : 0.04, total 67 μmol g⁻¹ h⁻¹), in addition to the normal CO hydrogenation products of alkenes, alkanes and ethanol (total 360 μmol g⁻¹ h⁻¹). The benzene clearly arises by a rhodium promoted hydrogenolysis, but the toluene, ethyl- and the higher alkylbenzenes come from the interaction of phenyl surface species with CH₂ derived from the CO. No styrene was detected, and when styrene was added to a Fischer–Tropsch run under the above conditions, it was completely hydrogenated to ethylbenzene.

p-Fluoroiodobenzene as initiator showed identical behaviour to iodobenzene and gave fluorobenzene, *p*-fluorotoluene and *p*-fluoro(ethyl)benzene in very similar ratios to those seen for iodobenzene. Such a reactivity pattern would *not* be expected if the individual steps involved the migration of aryl onto a rhodium-coordinated CO, since such processes are well known to be strongly inhibited by electron-withdrawing substituents on the migrating group. Thus the observation that the (relative and absolute) yields of products do not vary significantly between phenyl and *p*-fluorophenyl argues against a reaction in which the key step is a migration of the aryl onto coordinated CO. It is

highly significant that the parallel extends to the solution reactions and that the *p*-fluorophenyl dirhodium complex [((C₅Me₅)Rh(μ-CH₂))₂(*p*-FC₆H₄)(MeCN)]PF₆,[¶] also reacts under CO in the same way as its phenyl analogue **2**.^{||}

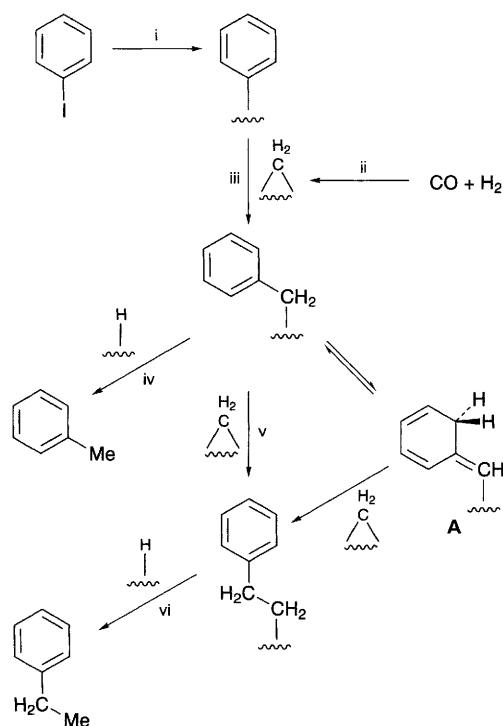
Scheme 3 proposes a reaction sequence for the formation of toluene on a surface. To make ethylbenzene (and the higher alkylbenzenes) from surface benzyl requires either the participation of surface species such as **A**, with unusual structures, or sp³–sp³ couplings. Neither alternative is likely to be energetically favourable, accounting for the low α (< 0.2) found for the formation of the alkylbenzenes by comparison to the alkenes.

Not only are the C₆H₅ and C₁ coupling reactions of the homogeneous dirhodium complex and the heterogeneous catalyst related, but there is also a clear parallel to reactions on single-crystal surfaces in high vacuum, where recent studies have shown that phenyl–metal (C₆H₅M) species are formed when copper(111) or silver(111) surfaces are reacted with C₆H₅I and C₆H₆ respectively, and that phenyl and methyl on silver react to give toluene.¹⁰

We conclude that surface phenyl on rhodium metal can behave very similarly to phenyl–rhodium in an isolated and characterised complex and that both can participate in similar types of C–C coupling processes.

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Scheme 3 Proposed mechanism for the production of toluene, and ethylbenzene from iodobenzene and CO + H₂. Formation of surface phenyl from iodobenzene (i) and of surface μ-CH₂ from CO plus H₂ (ii) respectively; coupling of phenyl and μ-CH₂ to give surface benzyl (iii), which can be hydrogenolysed to toluene (iv), or reacted with more μ-CH₂ either directly (v), or indirectly via **A**, to give phenylethyl on the surface which is hydrogenolysed to ethylbenzene (vi).

Footnotes

† Complex **2** (95% yield); Anal. Calc. for C₃₀H₄₂F₆NPRh₂: C, 46.9; H, 5.5; N, 1.8. Found: C, 46.6; H, 5.5; N, 1.7%. IR (KBr): ν/cm⁻¹ 2311w, 2297vw (MeCN), 840vs (PF₆). ¹H NMR [(CD₃)₂CO, -80 °C]: δ 1.40, 1.56 (2 x s, *cis*-C₅Me₅), 1.72, 1.76 (2 x s, *trans*-C₅Me₅), 2.64 (MeCN), 6.78 (d, 1H, *p*-Ph), 6.90 (t, 2H, *m*-Ph), 7.05 (d, 2H, *o*-Ph), 9.16, 9.31, 9.37, 9.75 (4 x m; *cis*- + *trans*-μ-CH₂). ¹³C NMR (CD₃COCD₃, -80 °C): δ 7.20, 7.79, 7.94, 7.99 (4 x s, C₅Me₅), 99.9, 101.0, 101.4, 102.0 [4 x d, *J*(Rh–C) 5 Hz, C₅Me₅], 121.4 (s, *m*-Ph), 126.5 (s, *o*-Ph), 136.7 (s, *p*-Ph), 154.0 [d, *J*(Rh–C) 40 Hz, *ipso*-C], 179.3 [t, *J*(Rh–C) 27 Hz, μ-CH₂].

‡ *trans*-**3**: ¹H NMR (CD₃COCD₃, -80 °C) δ 1.68, 2.02 (2 x s, *trans*-C₅Me₅), 6.93 (d, 1H, *p*-Ph), 6.98 (t, 2H, *m*-Ph), 7.26 (d, 2H, *o*-Ph), 9.12, 9.53 (2 x m, *trans*-μ-CH₂). On warming *trans*-**3** to +20 °C in an IR cell, a transient, ν(CO) appeared at 2046 cm⁻¹, that we propose arises from the *cis*-isomer.

§ One equivalent of acid is produced per equivalent of styrene. Part is consumed by the production of the other organics (e.g. benzene), and the concentration of acid remaining is too low to lead to observable perturbation of the first-order kinetic behaviour.

¶ The *p*-fluorophenyl analogue gave *p*-fluorostyrene (72%) and *p*-fluorotoluene (11%) on decomposition under CO. [((C₅Me₅)Rh(μ-CH₂))₂(*p*-FC₆H₄)(MeCN)]PF₆, (96% yield). Anal. Calc. for C₃₀H₄₄F₇NPRh₂: C, 45.9; H, 5.3; N, 1.8. Found: C, 45.6; H, 5.5; N, 1.7%. IR (KBr): ν/cm⁻¹ 2310w, 2290vw (MeCN), 838vs (PF₆). ¹H NMR (CD₃COCD₃, -60 °C): δ 1.36, 1.56, 1.62, 1.74 (4 x s, C₅Me₅), 2.60 (s, 3H, MeCN); 7.05 (m, 2H, *o*-Ph), 6.75 (m, 2H, *m*-Ph), 9.20, 9.32, 9.40, 9.80 (4 x m, *cis* + *trans*-μ-CH₂).

|| The methyl analogue [((C₅Me₅)Rh(μ-CH₂))₂(Me)(MeCN)]PF₆, reacted analogously in the presence of CO; however the reaction was much slower than for **2** and the main product was the ketone, MeCOCH₂Me, with less of the C–C coupling product, propene, being formed. The mechanism of the ketone formation has been commented on.¹¹

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