Phosphine–olefin ligands: a facile dehydrogenative route to catalytically active rhodium complexes†

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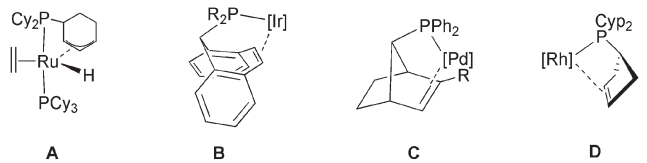
Facile, metal-mediated, (acceptorless) dehydrogenation of tricyclopentyl phosphine directly affords rhodium chelating phosphine–olefin complexes, some of which are catalytically active for 1,4-additions.

The selective activation and functionalisation of alkanes is one of the major goals in the field of organometallic chemistry.[1] A particularly useful case of alkane functionalisation is dehydrogenation to form alkenes. The dehydrogenation of alkanes usually requires either high temperatures or the use of a hydrogen acceptor.[2] In cases where the process is chelate assisted (intramolecular), mild conditions can be used for dehydrogenation. For example, Sabo-Etienne *et al.* have reported that treatment of the bis-dihydrogen complex $Ru(PCy_3)_2H_2(\eta^2\text{-}H_2)_2$ with ethene affords the cyclohexenyl complex $Ru(PCy_3)\{PCy_2(\eta^3\text{-}C_6H_8)\}H(\eta^2\text{-}H_2C{=}CH_2)$ **A**,[3] while Grützmacher *et al.* have reported that ligands based upon dibenzocycloheptyl phosphine undergo dehydrogenation on complexation with a metal centre, to give phosphine–olefin complexes such as **B**.[4]

The synthesis of mixed phosphine–olefin ligands is of significant interest.[4–7] Such ligands have been used by Hayashi *et al.* (**C** Scheme 1) in the catalysis of 1,4-addition reactions[6] and by Grützmacher in hydrogenation reactions.[7] However, the synthesis of such ligands is multistep and can be non-trivial. Here we report the straightforward and facile synthesis of a rhodium complex containing a phosphine–olefin ligand (**D**) by the dehydrogenation of a cyclopentyl group in the commercially available tricyclopentylphosphine ($PCyp_3$) ligand.[8] We also show that such complexes are effective catalysts for 1,4-addition reactions. That the active catalyst species is available in excellent yields and purity from readily available starting materials in two simple steps makes this methodology particularly attractive.

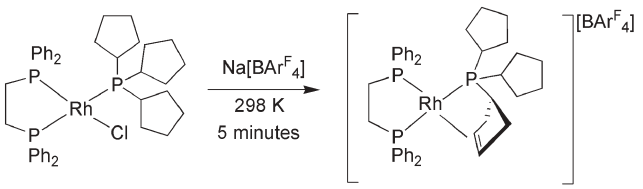
Treatment of $RhCl(dppe)(PCyp_3)$ with sodium tetrakis(1,3-bis(trifluoromethyl)phenyl)borate $\{Na[BAr^F_4]\}$ in CH_2Cl_2 results in dehydrogenation of one of the cyclopentyl rings and formation of the phosphine–olefin complex $[Rh(dppe)\{PCyp_2(\eta^2\text{-}C_5H_7)\}][BAr^F_4]$ (**1**) (Scheme 2). Remarkably, this dehydrogenation reaction occurs rapidly (minutes) at room temperature without a hydrogen acceptor and is quantitative (by NMR spectroscopy, see ESI). The reaction is also selective: only the 3,4-alkene is formed and reaction occurs on only one ring. The removal of the halide to generate a vacant site, subsequent C–H activation of the cyclopentyl ring *via* an agostic intermediate, β-elimination and finally H_2 loss is the most likely mechanism.[2]



Scheme 1

The assignment of (**1**) as a rhodium(I) complex containing a phosphine–olefin was made using NMR spectroscopy and single crystal X-ray crystallography.‡ The ^{1}H NMR spectrum shows a signal attributable to a coordinated alkene at δ 4.89, which shows one-bond correlation to a signal at δ 96.2 [dd, J 10 Hz, 9 Hz] in the ^{13}C NMR spectrum, fully consistent with a coordinated alkene. The ^{31}P NMR spectrum shows the expected three signals (see ESI), two with characteristically large *trans* P–P coupling [J(PP) 283 Hz]. In the solid-state (Fig. 1) the presence of a coordinated C=C double bond was confirmed by a short C–C distance [C3–C4 1.372(3) Å] together with M–C distances typical of M–olefin coordination [*viz.* 2.241(2), 2.242(2) Å]. Additionally (given the usual caveats regarding the location of hydrogens by X-ray diffraction), only one hydrogen for C3 and C4 respectively was located in the final difference map. The newly formed phosphine–olefin ligand has a bite angle (∠ P–Rh–centroid of C3/C4) of 84°, which is the same as that of dppe.

The intramolecular dehydrogenation of cyclopentane was also observed in other rhodium complexes. Treatment of $[Rh(nbd)Cl]_2$ with $PCyp_3$ gives $RhCl(nbd)(PCyp_3)$, which when treated with $Na[BAr^F_4]$ in fluorobenzene results in dehydrogenation and formation of the fluorobenzene complex $[Rh(\eta^6\text{-}C_6H_5F)\{PCyp_2(\eta^2\text{-}C_5H_7)\}][BAr^F_4]$ (**2**) (Scheme 3). Use of benzene as co-solvent gives the analogous benzene complex (**3**). In the formation of (**2**) and (**3**), the coordinated norbornadiene acts as a hydrogen acceptor, and norbornene is observed in the reaction mixture (by GC or ^{1}H NMR). The ^{1}H and ^{13}C{^{1}H} NMR spectra



(**1**)

Scheme 2

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† Electronic supplementary information (ESI) available: Experimental details, spectroscopic and crystallographic data for all the new compounds. See DOI: 10.1039/b608129k

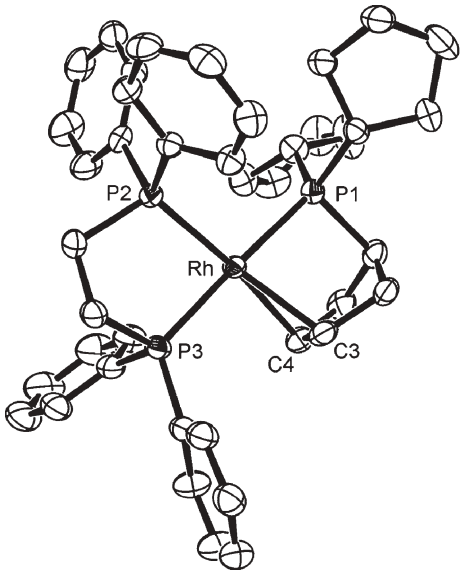
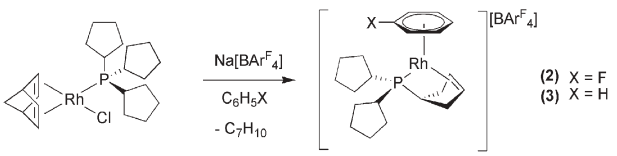


Fig. 1 ORTEP plot (50% ellipsoids) of the cationic portion of (**1**). Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Rh–P1 2.3284(5), Rh–P2 2.2818(5), Rh–P3 2.2709(5), Rh–C3 2.242(2), Rh–C4 2.241(2), C3–C4 1.372(3), P3–Rh–P2 83.823(19), P3–Rh–P1 174.42(2), P2–Rh–P1 100.068(19). Ct(3/4)–Rh–P3 93.01(6), Ct(3/4)–Rh–P2 172.15(6), Ct(3/4)–Rh–P1 83.63(6). Ct(3/4) is the centroid of the C3/C4 bond.



Scheme 3

of (**3**) show signals arising from the coordinated arene, together with a signal characteristic of a coordinated alkene [^{1}H: δ 4.3, ^{13}C: δ 62.72 d, J(RhC) 16 Hz, HC=CH]. Similar signals are observed in the spectra of (**2**). (**2**) and (**3**) have similar ^{31}P{^{1}H} NMR spectra, with (**2**) showing additional coupling due to the fluorine [J(FP) 3.8 Hz]. The solid-state structures (Fig. 2) confirm the presence of a coordinated C=C double bond by short C–C distances [(**2**) C13–C14 1.401(4); (**3**) C13–C14 1.414(5) Å] together with M–C distances typical of M–olefin coordination.

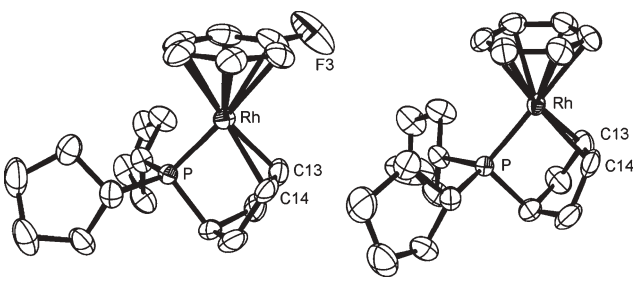


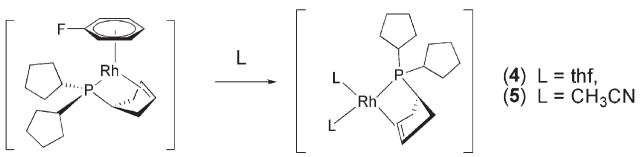
Fig. 2 ORTEP plot (50% ellipsoids) of the cationic portion of (**2**) (left) and (**3**) (right). Hydrogen atoms omitted for clarity. Selected bond lengths (Å) (**2**): Rh–P 2.2412(6), Rh–C13 2.125(2), Rh–C14 2.128(2), C13–C14 1.401(4); (**3**): Rh–P 2.219(3), Rh–C13 2.133(6), Rh–C14 2.114(4), C13–C14 1.414(5).

Complex (**2**) acts as a convenient source of the synthetically useful {PCyp$_2$(η^2-C$_5$H$_7$)Rh}$^+$ fragment, with other ligands displacing the weakly bound fluorobenzene. Reaction with benzene gives (**3**), while the reaction with two electron donors such as THF or CH$_3$CN gives the 16-electron, Rh(I), complexes [Rh{PCyp$_2$(η^2-C$_5$H$_7$)}L$_2$][BAr$^F_4$] [L = THF (**4**), MeCN (**5**), Scheme 4], which have been characterised by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy (see ESI).

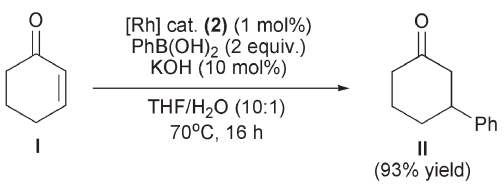
In previous studies, Hayashi *et al.* have established that hybrid phosphine–olefin ligands can offer distinct advantages over bidentate phosphine or diene ligands in the rhodium-catalysed 1,4-addition reaction.[6] The convenient preparation of (**2**) in only two steps from commercially available starting materials, coupled with the subsequent ease of fluorobenzene displacement makes it an attractive complex for use in catalytic studies. Thus, the 1,4-addition of phenylboronic acid to 2-cyclohexenone **I** was performed using 1 mol% of complex (**2**) as shown in Scheme 5.[9] The substrate was efficiently converted to the desired product **II**, which was isolated in 93% yield after column chromatography.

Having established that (**2**) is an effective catalyst for the 1,4-addition process, the chemoselectivity was investigated in a competitive 1,2- *versus* 1,4-addition reaction. The addition of phenylboronic acid to cinnamaldehyde **III** was examined at room temperature using 1 mol% of complex (**2**) as depicted in Scheme 6.

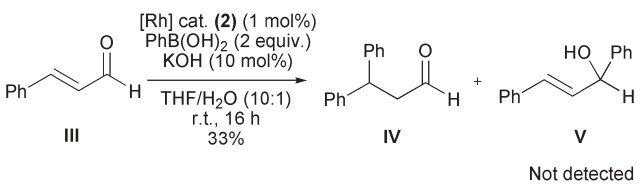
Interestingly, in the presence of (**2**) the 1,4-addition product **IV** was obtained exclusively. Although the conversion was modest at room temperature the 1,2-addition product **V** was not detected by ^{1}H NMR of the crude reaction mixture. The excellent chemoselectivity of (**2**) towards 1,4-addition is consistent with previous observations involving rhodium complexes with olefin ligands.[10] Miyaura *et al.* have noted the chemoselectivity switch to 1,2-addition in the presence of one equivalent of t-Bu$_3$P but the selectivity is sensitive to the choice of reaction conditions, with



Scheme 4

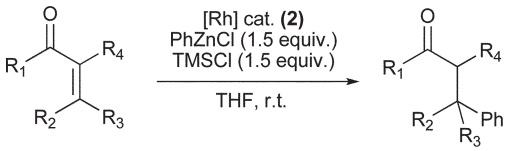


Scheme 5



Scheme 6

Table 1 Addition of phenylzinc chloride to activated alkenes catalysed by complex (**2**)[a]



Entry	R_1	R_2	R_3	R_4	(**2**) (mol%)	Reaction time (h)	Conversion[b] (Yield %)[c]
1	$-(CH_2)_3-$		H	H	1.0	2	100 (89)
2	$-(CH_2)_3-$		H	H	0.1	16	100
3	OMe	H	H	CH_2CO_2Me	1.0	2	100 (94)
4	OMe	H	H	CH_2CO_2Me	0.1	16	100
5	Ph	H	Ph	H	1.0	16	100 (85)

[a] All reactions are performed on 0.5 mmol of substrate. [b] Determined by ^{1}H NMR. [c] Isolated yield after column chromatography.

cationic rhodium complexes predominantly affording the 1,4-addition product.[11]

The utility of arylzinc nucleophiles in the rhodium-catalysed 1,4-addition reaction is known but to date there are relatively few examples.[12] To further explore the scope of (**2**) in 1,4-additions, the addition of phenylzinc chloride to 2-cyclohexenone **I**, dimethyl itaconate and chalcone was investigated and the results are shown in Table 1.

It is useful to note that water is not required for catalyst turnover when arylzinc reagents are employed in rhodium-catalysed 1,4-addition reactions.[12] The inert conditions are clearly beneficial to the catalytic activity of (**2**). In the addition to 2-cyclohexenone **I**, the reaction reached completion after 2 hours at room temperature with 1 mol% of catalyst and within 16 hours with just 0.1 mol% of catalyst (Table 1, entries 1–2). In a repeat of the addition with 1 mol% of catalyst, NMR analysis of the crude reaction mixture revealed the presence of the intact $\{PCyp_2(\eta^2\text{-}C_5H_7)Rh\}^+$ fragment in conjunction with complete conversion of **I** to the intermediate silyl enol ether. Furthermore, the catalyst species was still active. Upon the addition of a further 0.5 mmol of substrate and appropriate reactants, an overall 90% conversion was observed after 2 more hours.

An efficient 1,4-addition was also realised with the less reactive 1,1′-disubstituted alkene dimethyl itaconate.[13] As before, the addition of phenylzinc chloride to dimethyl itaconate was complete after 2 hours at room temperature with 1 mol% of (**2**) and within 16 hours in the presence of 0.1 mol% of (**2**) (Table 1, entries 3–4). Remarkably, the more challenging acyclic α,β-unsaturated ketone chalcone also undergoes complete conversion to the 1,4-addition product at room temperature with 1 mol% of (**2**) (Table 1, entry 5).[14]

In summary, a concise and practical synthesis of a rhodium complex containing a hybrid phosphine–olefin ligand is presented. That this occurs by a facile transfer dehydrogenation of a cyclopentyl group in $PCyp_3$ not only suggests future strategies for the synthesis of this important class of ligand, but also shows that $PCyp_3$ may not always act as a completely innocent ligand when complexed with a late-transition metal.

Notes and references

‡ *Crystallographic data*. Intensity data were collected at 150 K on a Nonius Kappa CCD, using graphite monochromated MoKα radiation (λ = 0.71073 Å). **1**: $C_{79}H_{66}BF_{25}P_3Rh$, M = 1696.95, monoclinic, space group $P2_1/c$ (Z = 4), a = 23.8390(2) Å, b = 13.11800(10) Å, c = 26.0540(2) Å, β = 113.06°. V = 7496.40(10) Å^3, μ = 0.398 mm^{-1}, $2\theta_{max}$ = 60°. 127183 reflections collected, 21803 unique [R(int) = 0.0666]. Final wR_2 = 0.1152 (all data), R_1 = 0.0416 [$I > 2\sigma(I)$]. **2**: $C_{53}H_{42}BF_{25}PRh$, M = 1298.56, monoclinic, space group $C2/c$ (Z = 8), a = 19.55500(10) Å, b = 16.35700(10) Å, c = 34.5800(2) Å, β = 106.38°, V = 10611.70(10) Å^3, μ = 0.477 mm^{-1}, $2\theta_{max}$ = 58.2°, 94762 reflections collected, 14840 unique [R(int) = 0.0633]. Final wR_2 = 0.0938 (all data), R_1 = 0.0428 [$I > 2\sigma(I)$]. **3**: $C_{53}H_{43}BF_{24}PRh$, M = 1280.56, monoclinic, space group $C2/c$ (Z = 8), a = 19.53700(10) Å, b = 16.43900(10) Å, c = 34.2820(2) Å, β = 106.53°, V = 10555.15(10) Å^3, μ = 0.476 mm^{-1}, $2\theta_{max}$ = 63°, 147742 reflections collected, 17437 unique [R(int) = 0.0475]. Final wR_2 = 0.0941 (all data), R_1 = 0.0365 [$I > 2\sigma(I)$]. CCDC 610374–610376. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608129k

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