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Bond activation by low valent ruthenium complexes

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Ru(η⁴-1,5-cyclo-octadiene)(η⁶-1,3,5-cyclo-octatriene) (1) is one of the most versatile zero-valent ruthenium complexes bearing two labile cyclopolyenes and acts as a potential precursor for catalytic processes involving bond cleavage reactions in the presence of suitable Lewis bases. However, detailed studies of the bond cleavage step had, until now, been relatively less explored at a molecular level. The present Perspective is an account of our recent studies concerning: (1) the reactions of 1 with Lewis bases, (2) carbon–oxygen, carbon–sulfur, oxygen–hydrogen, nitrogen–hydrogen and carbon–hydrogen bond cleavage reactions by 1 in the presence of tertiary phosphine, (3) selective sp³ carbon–hydrogen bond cleavage by 1 by use of coordination of an anchoring chalcogen atom, and (4) preparation of an enolatoruthenium(II) complex derived from 1 as an active intermediate in chemoselective catalytic Knöevenagel and Michael reactions.

1. Introduction

Ru(η⁴-1,5-COD)(η⁶-1,3,5-COT)[1] (**1**) is an attractive and versatile zero-valent ruthenium complex bearing two labile cyclopolyene ligands. It was prepared by E. O. Fischer and Müller for the first time in 1963 by the reaction of $RuCl_3$ with isopropyl Grignard reagent in the presence of 1,5-COD and 1,3,5-COT under exposure to UV light but the yield was quite poor.[2] Many research groups have been devoted to improving the synthesis of this attractive complex; Vitulli,[3] Itoh and Nagashima,[4] and Dahlenburg[5] finally developed a convenient reduction method by use of Zn metal making the practical yield up to 90%. **1** has been extensively employed in stoichiometric and catalytic reactions since the 1980s.[6] The historical background and applications of **1** were concisely reviewed previously.[7,8] Many unique catalyses involving bond cleavage have been developed by using the combination of **1** with suitable Lewis bases.[9] However, the role of the employed Lewis bases in the catalyses is not clearly understood to date. The major difficulties seem to be how to choose suitable Lewis bases for certain catalysis. This may be due to lack of knowledge of the reaction of **1** with Lewis bases in relation to activity towards the bond cleavage reaction at a molecular level, though some stoichiometric reactions of **1** with $P(OMe)_3$,[10,11] PMe_3,[10] DPPM,[10,12] alkynes[13] or CO[14] as well as arenes[15] or tertiary phosphines[16] under a hydrogen atmosphere have been documented as shown in Scheme 1.

Since the COT ligand is formally always displaced by the ligands added in these reactions, initial liberation of the COT from **1** has been believed to be the first step in both stoichiometric and catalytic reactions of **1** in the presence of Lewis bases, though mechanistic details were not studied at all in

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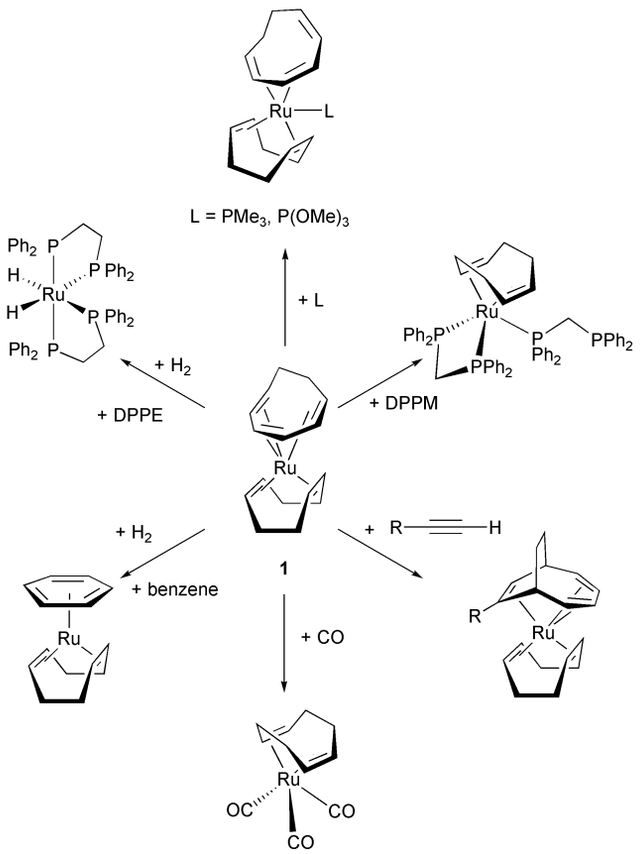


Scheme 1

many cases. This inquiry prompted us to investigate the stoichiometric reactions of **1** with a series of Lewis bases. Herein we report outcomes of our recent strategic studies concerning (1) systematic reactions of **1** with Lewis bases, (2) activation of C–O, C–S, C–H, N–H and O–H bonds by use of **1** in the presence of Lewis bases, (3) selective sp^3 C–H bond cleavage by **1** by use of chalcogen anchor, and (4) synthesis of enolato-ruthenium(II) complexes derived from **1** as active intermediates in catalytic Knöevenagel and Michael reactions.

2. Reactions of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (1) with Lewis bases

2.1. Reactions with mono-dentate tertiary phosphines

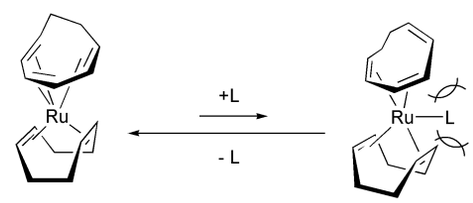
Since the steric and electronic factors of mono-dentate tertiary phosphines are well-defined by Tolman,[17,18] we looked at systematic reactions of **1** with a series of tertiary phosphines. Treatment of **1** with basic and compact monodentate phosphines such as PMe_3 or PMe_2Ph resulted in the immediate formation of the known mono phosphine adduct Ru(η^4-1,5-COD)(η^4-1,3,5-COT)L [L = PMe_3 (**2a**), PMe_2Ph (**2b**)], but further warming of **2a** or **2b** at 50 °C for 24–33 h led to the unexpected substitution reaction of the 1,5-COD ligand with these phosphines to form di-valent complexes Ru(6-η^1:1–3-η^3-COT)L_3 [L = PMe_3 (**3a**), PMe_2Ph (**3b**)] in 25–42% isolated yields, respectively (Scheme 2).[19,20]

These complexes **3a**–**b** were fully characterised with their X-ray structure analyses. The molecular structure of **3b** is depicted in Fig. 1 showing the unambiguous η^1:η^3-co-ordination mode of the COT moiety.

Three PMe_2Ph ligands co-ordinate to the two equatorial and one apical sites in the trigonal bipyramidal geometry. The η^1:η^3-co-ordination mode of the COT ligand should remain intact even in solution because the characteristic allylic resonance as well as the diastereotopic geminal methyl groups in the PMe_2Ph ligand are clearly apparent in the ^1H NMR spectrum.

Of particular interest are the reactions of **1** with basic but moderately bulky phosphines such as PEt_3, PBu_3 and PEt_2Ph. These reactions at 50 °C also led to the substitution reaction of the 1,5-COD ligand by phosphines *via* corresponding mono phosphine intermediates **2c**–**e**, to give zero-valent complexes Ru(η^4-1,3,5-COT)L_3 [L = PEt_3 (**4c**), PBu_3 (**4d**), PEt_2Ph (**4e**)].[21] The molecular structure of **4c** is illustrated in Fig. 1 showing an η^4-co-ordination of the 1,3,5-COT ligand. In solution these complexes constitute an equilibrium between **4** and (η^5-cyclo-octatrienyl)(hydrido)ruthenium(II) **5** (*e.g.* **4c** : **5c** = 8 : 1 at 25 °C), which was given by the liberation of one of the phosphine ligands followed by the intramolecular C–H bond oxidative addition of the 1,3,5-COT ligand. This fact suggests that **4** is potentially more active toward bond cleavage reactions than **3**, since such a simple η^4-1,3,5-COT tends to dissociate more easily than η^1:η^3-COT. The variable temperature NMR spectra of **5c**–**e** suggest the presence of at least two isomers at low temperature. They are most likely the rotamers by rotation of the $RuHL_2$ moiety as reported for RuCl(η^5-C_8H_9)$(PPh_3)_2$[22] or RuCl(η^5-C_7H_9)$(PPh_3)_2$.[23]

On the other hand, similar treatment of **1** with more bulky phosphines such as PPh_3, P^iPr_3, and PCy_3 gave no reaction at all. Without exception, all reactive tertiary phosphines quickly formed mono phosphine adduct **2** at first, followed by the formation of **3** or **4** in the reaction with **1**. Therefore, formation of the mono phosphine adduct is considered as the entry step for further reactions. The inactivity of these bulky phosphines is likely due to the negligible formation constant of the mono phosphine adduct because of the large steric hindrance among the phosphine and cyclopolyenes in **2** [eqn. (1)].

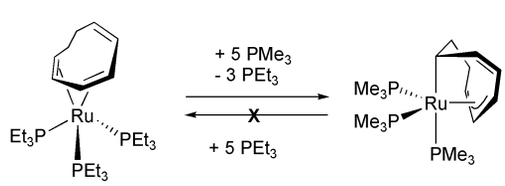


(1)

1 **2**

L = PPh_3, P^iPr_3, PCy_3

As described above, tertiary phosphines do not displace the COT ligand, but unexpectedly liberate the COD ligand to give the complex formulated as Ru(COT)L_3, in which the formal oxidation state is *two* for more compact and electron donating ligands to give a 6-η^1:1–3-η^3-COT co-ordination mode, but is *zero* for PEt_3, PBu_3, and PEt_2Ph to give η^4-1,3,5-COT. It is worth noting that reaction of **4c** with 5 equiv. of PMe_3 almost quantitatively displaces PEt_3 to PMe_3, during which the co-ordination mode of the cyclo-octatriene ligand has changed from η^4 to η^1:η^3 without formation of any detectable intermediate [eqn. (2)].[24]

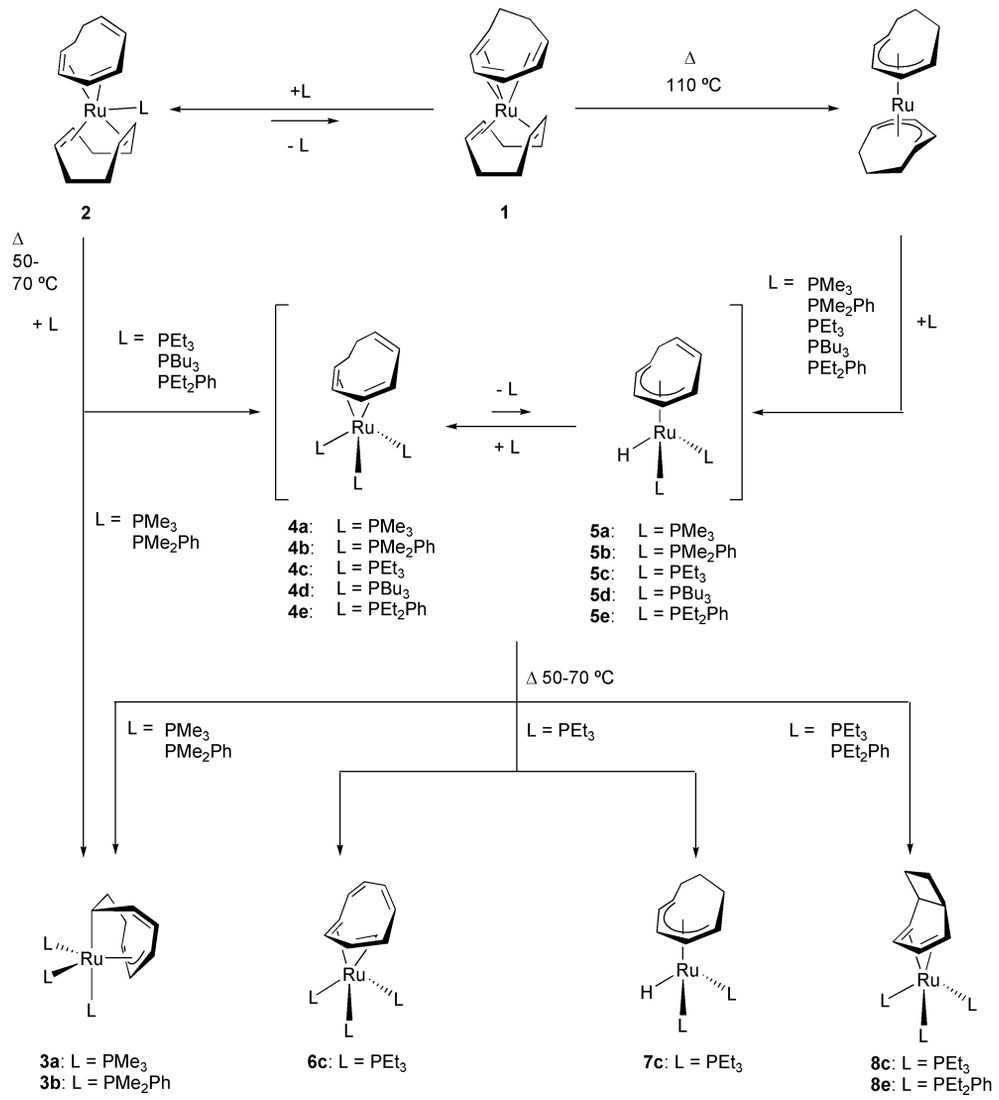


(2)

4c **3a**

93%

This haptotropic change clearly indicates that the metal valency is controlled not by the basicity but the steric factor of the phosphine employed. On the other hand, the reverse reaction, from **3a** to **4c**, did not proceed at all. Thus, we can conclude that the divalent η^1:η^3-COT co-ordination with PMe_3 ligands is thermodynamically favourable.



Scheme 2

The thermodynamically less stable η⁴-1,3,5-COT complexes **4** showed further transformation of the polyene ligand. Heating of **4c** at 70 °C for 100 h led to the disproportionation reaction giving a mixture of a cyclo-octatetraene complex Ru(η⁴-cyclo-octatetraene)$(PEt_3)_3$ (**6c**) and a (cyclo-octadienyl)(hydride)-ruthenium(II) complex $RuH(\eta^5\text{-}C_8H_{11})(PEt_3)_2$ (**7c**) in a 1 : 1 ratio (Scheme 2), from which **6c** was unequivocally isolated by preferential crystallisation as shown in Fig. 1.[21] Complex **6c** shows a sharp singlet in the $^{31}P\{^1H\}$ NMR and the cyclo-octatetraene moiety resonates as a sharp singlet in the ^1H NMR in benzene-d_6 at 20 °C, but the cyclo-octatetraene resonance gradually broadened on cooling and collapsed into the base-line at −80 °C in toluene-d_8, while no significant change was observed for other signals. Thus, the cyclo-octatetraene moiety in complex **6c** is considered to rotate on the $Ru(PEt_3)_3$ fragment as reported for the analogous cyclo-octatetraene complexes such as Ru(η⁴-C_8H_8)(hexamethylbenzene)[25] or Ru(η⁴-C_8H_8)-$(CO)_3$.[26]

As described above, heating of isolated **4c** at 70 °C leads to the disproportionation reaction. However, heating of the mixture of **1** with PEt_3 or PEt_2Ph under the same conditions for a longer period mainly caused intramolecular cyclisation of the cyclo-octatriene ligand into the bicyclic one to form Ru(η⁴-bicyclo[4.2.0]octa-2,4-diene)$(PEt_3)_3$ (**8c**) (or **8e**) in 67% yield *via* the η⁴-1,3,5-COT intermediate **4c** (or **4e**).[21] The molecular structure of the PEt_2Ph analogue **8e** is depicted in Fig. 1. The bond distance C(5)–C(8) [1.531(9) Å] unambiguously indicates a typical C–C single bond showing formation of bicyclo[4.2.0]octa-2,4-diene ligand. When the isolated **4c** was heated at 70 °C for 3 days in the presence of 1,5-COD or PEt_3, complex **8c** was mainly formed, while simple heating of **4c** gave **6c** and **7c** by disproportionation. The result suggests that the fate of the 1,3,5-COT moiety is controlled by the presence 1,5-COD or PEt_3. On the other hand, substitution reaction of a cyclo-octatetraene in **6c** by free 1,3,5-COT also smoothly took place to produce a bicylo[4.2.0]octa-2,4-diene complex **8c** in 100% yield at 70 °C for 4.5 h without formation of any detectable intermediate.[24] It is also necessary to consider that free 1,3,5-COT consists of an equilibrium mixture of 1,3,5-COT and a small amount of bicyclo[4.2.0]octa-2,4-diene in solution.[27] By taking into account of these facts, the bicyclic diene is considered to eventually co-ordinate to ruthenium due to its higher thermodynamic stability than the other cyclic polyene ligand probably because of the effective strain relief of the bicyclic ligand on co-ordination. Thus, we can conclude that once the 1,3,5-COT moiety was released from **4c** by the assistance of an appropriate ligand such as 1,5-COD or external PEt_3, only the isomerised bicyclo[4.2.0]octa-2,4-diene preferentially co-ordinated to the ruthenium to form **8c** (Scheme 3).[28,29]

2.2. Reaction of Ru(η⁴-1,5-COD)(η⁶-1,3,5-COT) (1) with bi- and tri-dentate phosphines

Chaudret and co-workers reported the reactions of **1** with DPPM to form Ru(η⁴-1,5-COD)(DPPM-κ²*P*,*P*′)(DPPM-κ¹*P*).[12] We re-investigated the analogous reaction of **1** with

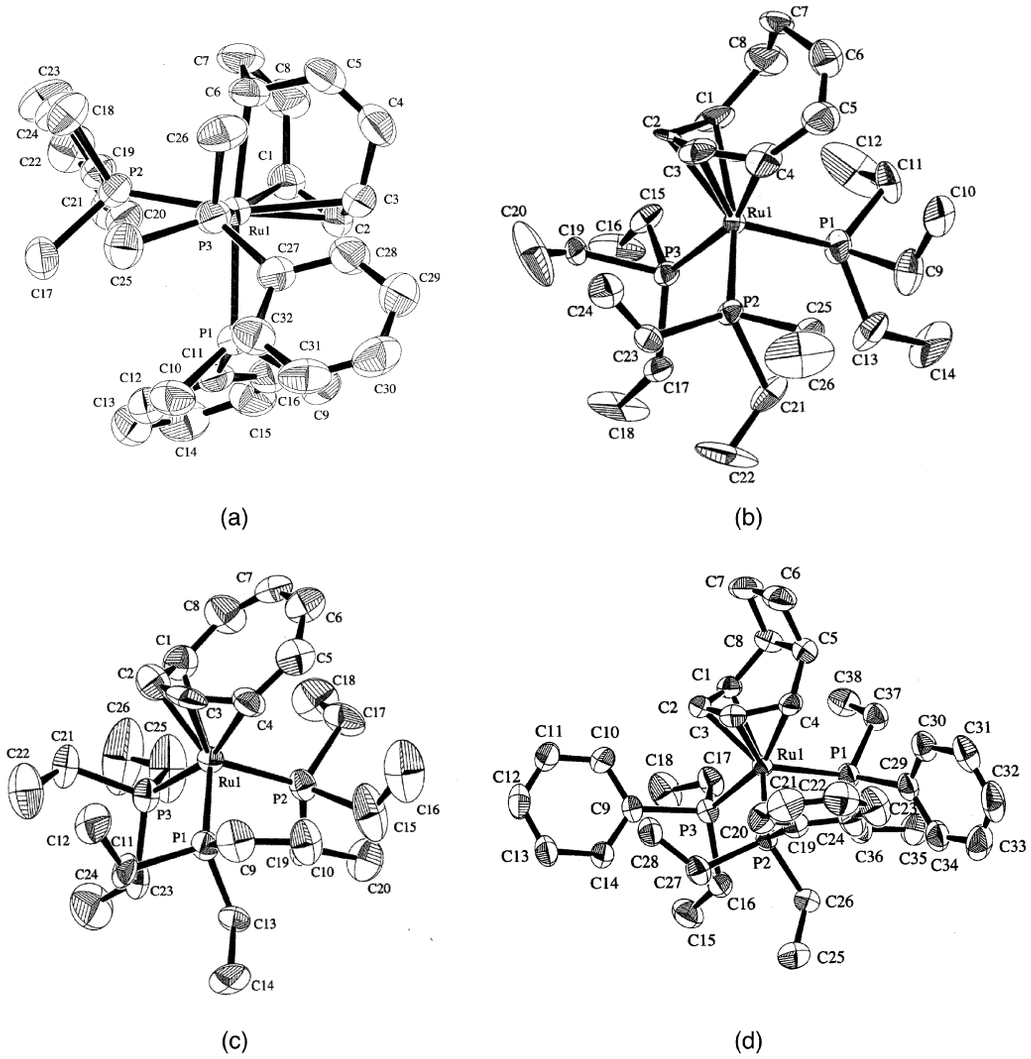
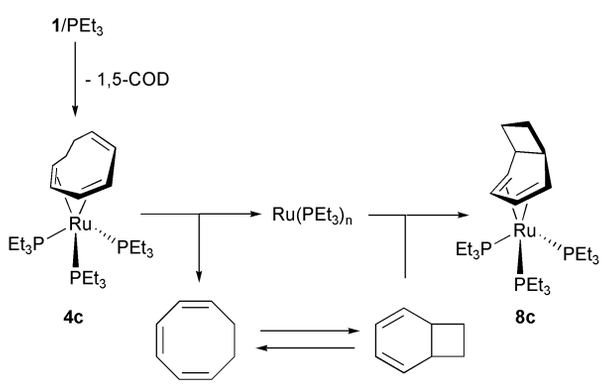


Fig. 1 Molecular structures of mono dentate phosphine complexes derived from **1**. (a) Ru(6-η^1:1–3-η^3-COT)(PMe_2Ph)$_3$ (**3b**). (b) Ru(η^4-1,3,5-COT)(PEt_3)$_3$ (**4c**). (c) Ru(η^4-cyclo-octatetraene)(PEt_3)$_3$ (**6c**). (d) Ru(η^4-bicyclo[4.2.0]octa-2,4-diene)(PEt_2Ph)$_3$ (**8e**).



Scheme 3

ethylene bridged bidentate tertiary phosphines such as DMPE and DEPE. The reactions of **1** with 2 equiv. of DMPE and DEPE initially formed Ru(η^4-1,5-COD)(η^4-1,3,5-COT)(bidentate phosphine-κ^1P) (**2f**,**g**), which then yielded Ru(η^4-1,5-COD)(DMPE-κ^2P,P')(DMPE-κ^1P) (**9f**) or Ru(η^4-1,5-COD)-(DEPE-κ^2P,P')(DEPE-κ^1P) (**9g**) at 50 °C for 2.5 h in 18 and 49% yields respectively, by the selective release of 1,3,5-COT (Scheme 4).[19]

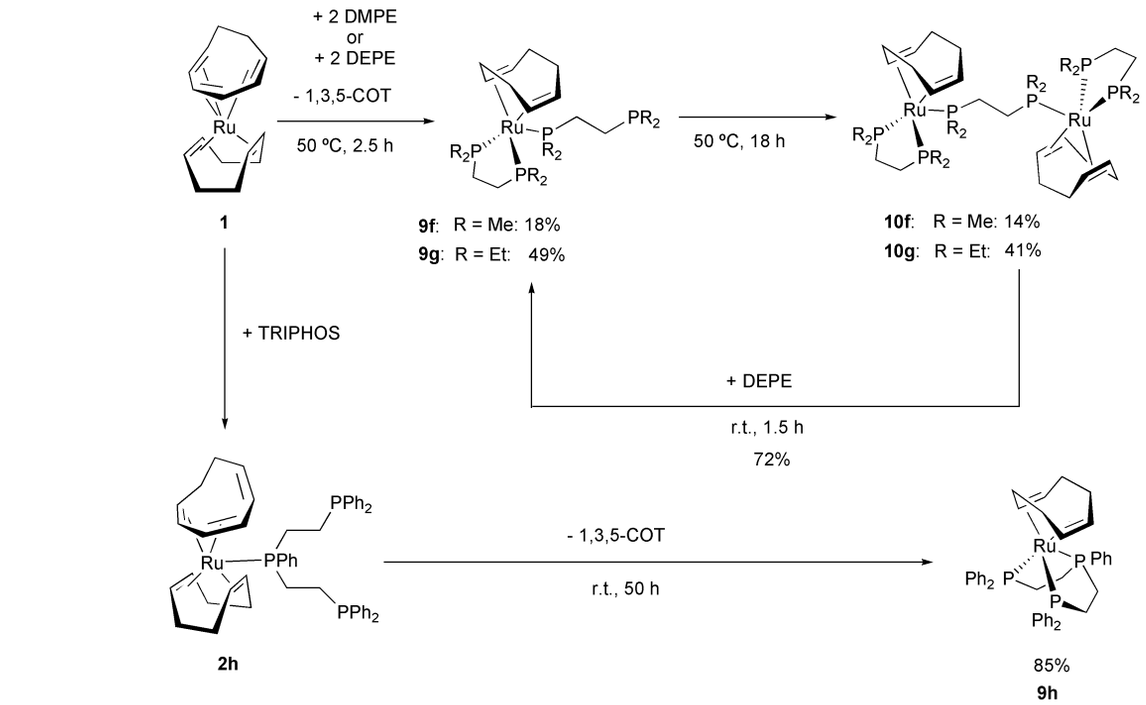
They are basically similar complexes to those reported by Chaudret,[12] but further heating of **9** at 50 °C for 18 h gave an analytically pure dinuclear complex [Ru(η^4-1,5-COD)(DMPE-κ^2P,P')]$_2$(μ-DMPE-κ^2P,P') (**10f**) and [Ru(η^4-1,5-COD)(DEPE-κ^2P,P')]$_2$(μ-DEPE-κ^2P,P') (**10g**) in 14 and 41% yields, respectively. However, addition of DEPE to **10g** at room temperature for 1.5 h reproduced **9g** in 72% yield.

When complex **1** reacts with a tridentate phosphine TRIPHOS, the least hindered central phosphine of the TRIPHOS initially co-ordinates to the ruthenium centre to form Ru-(η^4-1,5-COD)(η^4-1,3,5-COT)(TRIPHOS-κ^1P^1) (**2h**), and then further reaction at room temperature for 50 h resulted in the formation of a 1,5-COD complex, Ru(η^4-1,5-COD)(TRIPHOS-$\kappa^3P^1,P^2,P^{2'}$) (**9h**) in 85% yield by concomitant liberation of 1,3,5-COT ligand (Scheme 4).[30] The five-co-ordinate complex **9h** shows a fluxional behaviour in solution due to rapid rotation of the 1,5-COD ligand at room temperature.

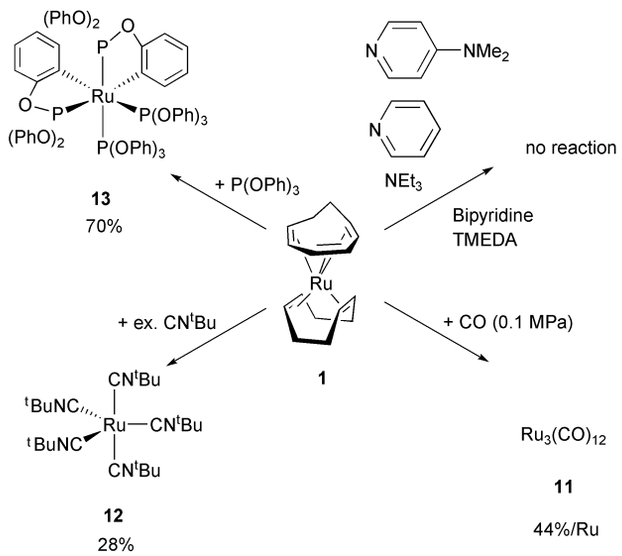
As shown above, bi- and tri-dentate phosphines selectively displace the 1,3,5-COT ligand in **1** to form the corresponding zero-valent 1,5-COD complexes.

2.3. Reaction with other σ-donors

Contrary to the phosphine ligands, **1** did not react at all with nitrogen donors such as NEt_3, pyridine, 4-dimethylaminopyridine (DMAP), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, and 2,2′-bipyridine. These nitrogen donors are generally considered as good σ-donors but poor π-acceptors,[31] while phosphine donors behave as good π-acceptors as well because of their low-lying σ* (and d) orbitals.[32] Therefore, this fact suggests that **1** acts as a π-base reflecting the zero-valent d^8 properties. Consistently, **1** readily reacted with π-accepting ligands such as CO, CN^tBu or $P(OPh)_3$ as shown in Scheme 5.[33]



Scheme 4



Scheme 5

As reported by Sandrini and co-workers,[14] treatment of **1** with CO initially gave a mono carbonyl complex Ru(η⁴-1,5-COD)(η⁴-1,3,5-COT)(CO) (**2i**). Further reaction gave Ru(6-η¹:1–3-η³-COT)$(CO)_3$ (**3i**) and Ru(η⁴-1,5-COD)$(CO)_3$ (**9i**) with concomitant formation of 1,3,5-COT followed by eventual formation of $Ru_3(CO)_{12}$ (**11**) in 44% yield.

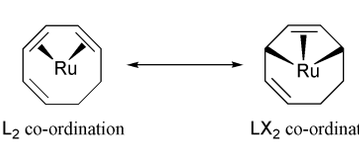
Similar treatment of **1** with CNᵗBu initially gave a mono isonitrile complex Ru(η⁴-1,5-COD)(η⁴-1,3,5-COT)(CNᵗBu) (**2j**) and then yielded a COD complex Ru(η⁴-1,5-COD)$(CN^tBu)_3$ (**9j**) in 58% yield with liberation of 1,3,5-COT.[33,34] The molecular structure of **9j** shows that one of the isonitrile ligands has significant contribution as carbene reflecting strong back donation from the Ru(0) centre. Unexpectedly, the prolonged reaction displaced the 1,5-COD ligand in **9j** by 1,3,5-COT to liberate 1,5-COD to form Ru(6-η¹:1–3-η³-COT)$(CN^tBu)_3$ (**3j**) in 56% yield. Addition of free CNᵗBu to the reaction mixture effectively suppressed the process of **9j** to **3j** suggesting the prerequisite dissociation of CNᵗBu ligand in **9j** giving a co-ordinatively unsaturated species for the reaction. Thus, **9j** and **3j** are considered as kinetic and thermodynamic products, respectively. Further treatment of **9j** with excess CNᵗBu gave a homoleptic complex $Ru(CN^tBu)_5$ (**12**) in 28% yield.[35]

Treatment of **1** with $P(OPh)_3$ also gave Ru(η⁴-1,5-COD)(η⁴-1,3,5-COT)$\{P(OPh)_3\}$ (**2k**) at the initial stage, which then gave a mixture of Ru(η⁴-1,5-COD)$\{P(OPh)_3\}_3$ (**9k**), and Ru(6-η¹,η³-COT)$\{P(OPh)_3\}_3$ (**3k**).[33] Further treatment of these complexes with excess amount of $P(OPh)_3$ resulted in the orthometallation to give $\overline{Ru\{P(OC_6H_4)(OPh)_2\}_2}\{P(OPh)_3\}_2$ (**13**)[36] with evolution of hydrogen gas, probably *via in situ* formed homoleptic complex $Ru\{P(OPh)_3\}_n$.

One of the interesting features is the ligand displacement of 1,5-COD by liberated 1,3,5-COT when strong π-accepting Lewis bases are employed. This may be because of the weaker co-ordination ability of 1,3,5-COT, compared to 1,5-COD, to induce initial liberation of 1,3,5-COT, but the thermodynamic stability of the 6-η¹:1–3-η³-COT co-ordination mode eventually led to the formation of **3j** or **3k**. In any case, these reactions finally afforded homoleptic complexes.

2.4. General features for the reaction of 1 with Lewis bases

Though detailed controlling factors concerning the ligand displacement reactions of **1** with Lewis bases have been described elsewhere,[33] it is interesting to briefly summarise the reaction trend in which cyclic polyene ligands are displaced. For monodentate Lewis bases, strong and compact donors favour loss of the COD ligand giving an $Ru(COT)L_3$ type complex, but strong π-acceptor ligands such as triarylphosphite, isonitrile and CO basically cause liberation of the COT ligand. The selectivity is conveniently interpreted by considering the stability of cyclic polyene ligands in mono-phosphine adduct **2** in the following way. The more electron-donating ligands such as tertiary phosphines reduce the ruthenium centre to cause efficient back bonding to cyclic polyene ligands. Thus, the LX_2 (or $\pi\sigma_2$) contribution in the COT ligand, as shown in eqn. (3), increases to stabilise the bonding between COT and Ru.



(3)

Table 1 Summary for the reaction of **1** with trialkylphosphite, phosphonite, and phosphinites[a]

Ligand	Cone angle/°	Conversion (%)	Yield (%) **3**	Yield (%) **4**
$P(OMe)_3$	107	100	44	49
$P(OEt)_3$	109	100	36	40
$P(OMe)_2Ph$	115	100	13	61
$P(OEt)_2Ph$	116	100	11	77
$P(O^iPr)_3$	130	100	8	48
$P(OMe)Ph_2$	132	100	17	53
$P(OEt)Ph_2$	133	100	16	42

[a] Conditions: **1** (0.049–0.0720 mmol), phosphorus compound (3 equiv.), C_6D_6 (0.6 mL), 50 °C, 20–24 h.

Such influence is considered to be larger in COT than in COD, since back bonding may be more efficient for the conjugated π-system than the nonconjugated one. On the other hand, if L is highly electron withdrawing such as isonitrile, electron density at Ru considerably decreases. Therefore, the LX_2 (or $\pi\sigma_2$) contribution in the COT ligand diminishes.

Differences in the co-ordination mode of the COT ligand in products is an another matter for discussion. For mono-dentate tertiary phosphine ligands, treatments of **1** with them alternatively gave either Ru(6-η^1:1–3-η^3-COT)L_3 (**3**) or Ru(η^4-1,3,5-COT)L_3 (**4**) depending on their steric bulkiness. The product ratio in the cases of trialkylphosphite, phosphonite and phosphinite ligands also shows that the ratio of **4** to **3** tends to decrease with decrease in the cone angle of L as shown in Table 1.

The complete displacement of the ligand may arise from their extremely strong π-accepting property neutralising the highly reduced zero-valent ruthenium centre. In the case of $P(OAr)_3$ further oxidation takes place to give an orthometallation product. On the other hand, the reactions of **1** with bi- and tri-dentate phosphine ligand resulted in the formation of zero-valent complexes.

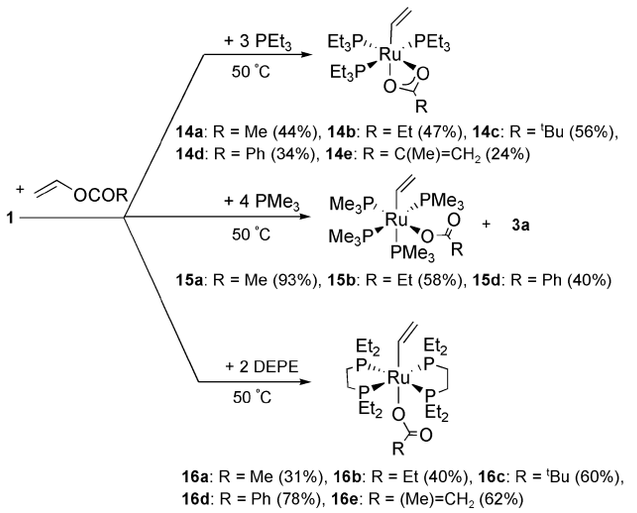
3. Carbon–oxygen or –sulfur bond cleavage reactions

The carbon–oxygen bond cleavage reaction is one of the key inlets in environmentally benign non-halogen catalysis. Especially, formation of allyl- and vinyl-ruthenium(II) complexes from corresponding esters and ethers are of particular interest in relation to ruthenium-based catalysis.[7] Whereas oxidative additions of C–O bonds in allylic esters to palladium complexes have been well established,[37] explicit examples of oxidative addition to ruthenium were unprecedented until one of the authors published the first report concerning vinylic C–O bond cleavage.[38] Such a comprehensive study would provide fundamental information for ruthenium-catalysed molecular transformations of esters and ethers. Our recent results concerning the oxidative addition of C–O and C–S bonds of alkenyl esters, ethers, and sulfides are described below. C–H and N–H bond activation reactions of thiophenes, furans and pyrrole derivatives are also mentioned.

3.1. Vinylic carbon–oxygen or –sulfur bond cleavage

Treatment of **1** with vinyl acetate in the presence of PEt_3 resulted in the oxidative addition of the C–O bond to give an octahedral vinylruthenium(II) complex, *mer*-Ru(C_2H_3)(OC-OMe-κ^2*O*,*O*′)(PEt_3)$_3$ (**14a**) (Scheme 6).[39]

When the more compact mono-dentate phosphine, PMe_3, was employed in this reaction, *cis*-(κ^1-acetato)(vinyl)-ruthenium(II) complex **15a** was produced with concomitant formation of **3a**. It is notable that addition of PMe_3 to **14a** also gave **15a** in quantitative yield. On the other hand, *trans*-(κ^1-



Scheme 6

acetato)(vinyl)ruthenium(II) complex **16a** was formed by the reaction of **1** with vinyl acetate in the presence of DEPE. Thus, the co-ordination ability of the ancillary ligand seems to determine the configuration of the (carboxylato)(vinyl)ruthenium(II) complexes. It is generally accepted that the highly reduced phosphine complexes show high activity toward bond cleavage reactions by oxidative addition. Thus, we have studied the performance of the ruthenium phosphine complexes described above, which were obtained by the reactions of **1** with tertiary phosphines, toward the reaction with vinyl ester. In fact, reaction of **4c** with vinyl propionate in benzene-d_6 rapidly gave (propionato)(vinyl)ruthenium(II) complex **14b** in 89% yield. The time–yield curves for the reaction are illustrated in Fig. 2. For comparison, the reaction using **1** in the presence of 3 equiv. of PEt_3 under the same conditions is also shown.

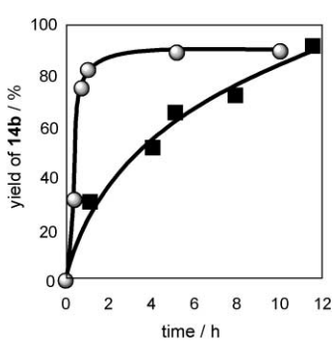
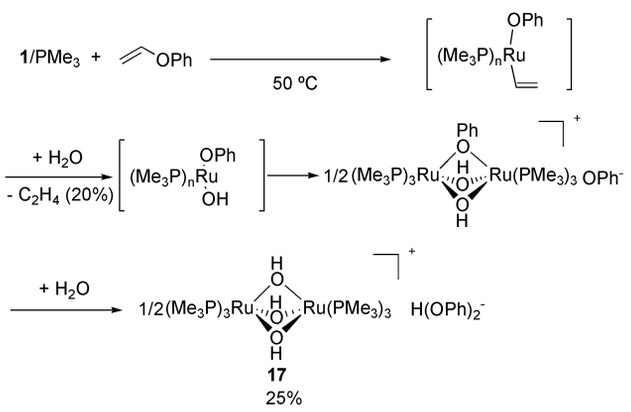


Fig. 2 Time-course curves for the oxidative addition of vinyl propionate to Ru(η^4-1,3,5-COT)(PEt_3)$_3$ (**4c**) (circle) and to Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**) with 3 equiv. of PEt_3 (square) at 50 °C in benzene-d_6. [Ru] = 0.075 mM.

The rate for the formation of **14b** from zero-valent complex **4c** is undoubtedly faster than that from **1** with 3 equiv. PEt_3 under the same reaction conditions.[20] Thus, **4c** is regarded as an intermediate for the C–O bond cleavage reaction and the rate-determining step is the formation of **4c** when the reaction starts from **1**. On the other hand, di-valent complex **3a** did not react with vinyl propionate. Since the Lewis basicity between PEt_3 and PMe_3 is comparable,[18] this significant difference in the oxidative addition is considered to reflect the difference in their formal oxidation state. As shown in Scheme 6, the vinylic C–O bond can in fact be cleaved by the combination of **1**/PMe_3. In this case, the ruthenium(0) species is probably formed *in situ* to proceed the C–O bond cleavage reactions. Inspection of the time-course for the reaction of **1**/DEPE with vinyl propionate gave some important information. Three sets of diastereomeric mixtures of zero-valent complexes, Ru(η^2-C_2H_3OCOEt)(η^4-1,5-

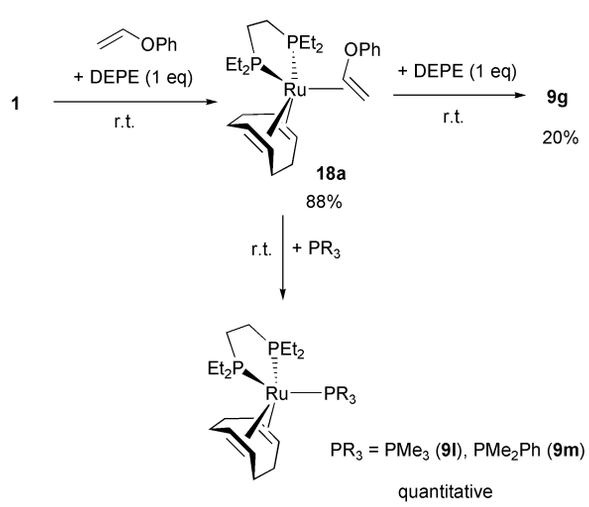
COD)(DEPE) were detected prior to the formation of **16b**.[39] Such diastereomeric products have been isolated in the reaction with phenyl vinyl ethers (*vide infra*). These results suggest the importance of co-ordination *via* the C=C double bond to ruthenium to cause the C–O bond oxidative addition.

Contrary to the reactions of vinyl esters, treatment of **1**/PMe_3 with phenyl vinyl ether gave a cationic tri(μ-hydroxo)di-ruthenium complex $[\{Ru(PMe_3)_3\}_2(\mu\text{-}OH)_3][OPh]\cdot HOPh$ (**17**·HOPh) with evolution of ethylene.[40] An analogue of **17** has been independently prepared from $\{Ru(PMe_3)_3\}_2(\mu\text{-}CH_2)_3$ and Ph_3CBF_4 in THF by Wilkinson and co-workers.[41] When the reaction was carried out in the presence of D_2O, the evolved gas consisted of only ethylene-d_1. Thus, the reaction probably proceeded by initial oxidative addition of vinylic C–O bond in vinyl phenyl ether followed by rapid hydrolysis of the resulting vinyl and phenoxo moieties by the small amount of incorporated water as shown in Scheme 7.



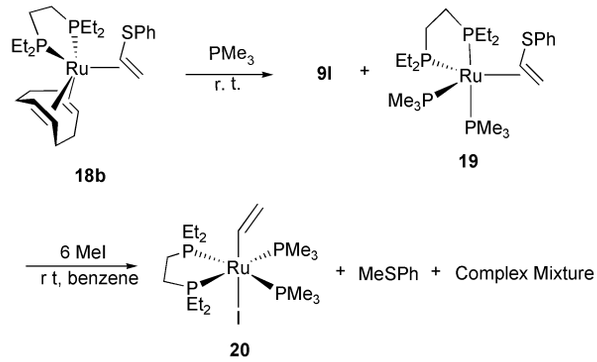
Scheme 7

When a bi-dentate phosphine, DEPE, was employed in this reaction a diastereomeric mixture of η^2-(phenyl vinyl ether) complexes $Ru(\eta^2\text{-}C_2H_3OPh)(\eta^4\text{-}1,5\text{-}COD)(DEPE\text{-}\kappa^2P,P')$ (**18a**) was obtained (Scheme 8).[39]



Scheme 8

The binding force for phenyl vinyl ether to ruthenium is weak and it was readily displaced by the added PMe_3, PMe_2Ph or DEPE to give the corresponding COD complex **9g**, **9l** and **9m** at room temperature. Thus, no C–O bond cleavage reactions took place in these cases. The similar complex $Ru(\eta^2\text{-}C_2H_3SPh)(\eta^4\text{-}1,5\text{-}COD)(DEPE\text{-}\kappa^2P,P')$ (**18b**) was also obtained by the reaction with phenyl vinyl sulfide. Treatment of **18b** with PMe_3 led to the formation of **19** with concomitant formation of **9l** (Scheme 9).

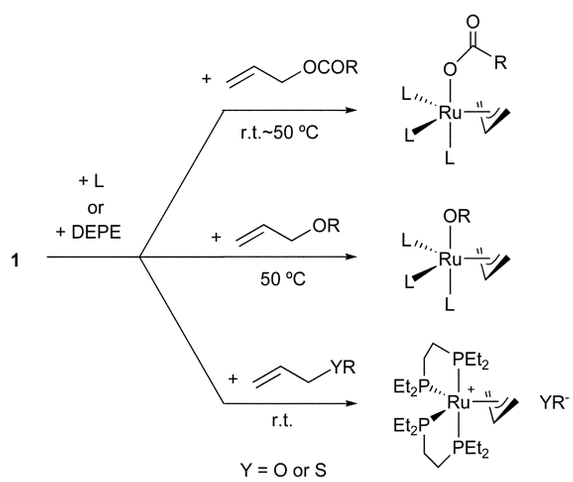


Scheme 9

Addition of MeI to the mixture involving **19** resulted in C–S bond cleavage to give a vinyl complex *trans*,*cis*,*cis*-$Ru(C_2H_3)(I)(DEPE\text{-}\kappa^2P,P')(PMe_3)_2$ (**20**) and MeSPh. We believe that the C–S bond cleavage takes place by direct electrophilic attack of MeI to the co-ordinated phenyl vinyl sulfide as we have shown for thiophenes and benzothiophenes (*vide infra*).

3.2. Allylic carbon–oxygen or –sulfur bond cleavage

C–O Bond in allylic carboxylates was also readily cleaved by oxidative addition to give the corresponding η^3-allyl-ruthenium(II) complexes (Scheme 10).[20,42]



Scheme 10

Although competitive hydrolysis by trace water in the system led to the evolution of propylene, a series of η^3-allylic complexes were isolated when strictly dried solvents were used (Table 2).

It is notable that both reactions using 1-methylallyl and 2-butenyl esters resulted in the formation of the same *syn*-η^3-methylallyl complex. However, the oxidative addition of 1-methylallyl ester was significantly slower than that of allyl or 2-butenyl ester. Neither 2-methylallyl nor 3-methyl-2-butenyl ester gave the allylruthenium(II) complex. Thus, two or more substituents at the C=C double bond strongly discourage the reaction. These facts suggest the importance of the prior co-ordination of the C=C bond as shown for vinyl ester for the oxidative addition of the allylic C–O bond. Similarly, C–O and C–S bonds in allylic ethers and sulfide were also cleaved to give η^3-allyl complexes.[43]

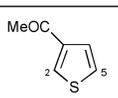
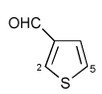
3.3. Carbon–sulfur bond cleavage of substituted thiophenes

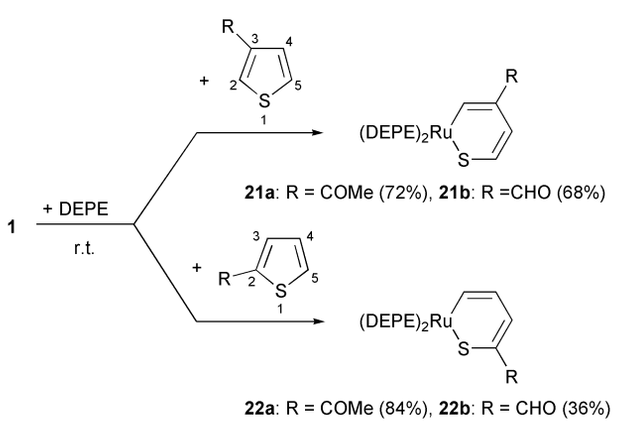
Carbon–sulfur bond cleavage reactions of thiophenes are also of interest in relation to hydrodesulfurisation of fossil oil for petroleum and lubricant.[44] Complex **1** is also susceptible to regioselective C–S bond cleavage of substituted thiophene in the presence of DEPE (Scheme 11).[45] It is notable that

Table 2 Oxidative addition of allylic carboxylate, ether and sulfide to Ru(1,5-COD)(1,3,5-COT) (**1**) in the presence of tertiary phosphine

Phosphine (mol Ru^{-1})	Substrate	Product	Yield (%)
3 PEt_3	CH_2=$CHCH_2OCOCF_3$	$Ru(\eta^3\text{-}C_3H_5)(OCOCF_3)(PEt_3)_3$	21
3 PMe_3	CH_2=$CHCH_2OCOCF_3$	$Ru(\eta^3\text{-}C_3H_5)(OCOCF_3)(PMe_3)_3$	64
3 PMe_2Ph	CH_2=$CHCH_2OCOCF_3$	$Ru(\eta^3\text{-}C_3H_5)(OCOCF_3)(PMe_2Ph)_3$	49
3 $PMePh_3$	CH_2=$CHCH_2OCOCF_3$	$Ru(\eta^3\text{-}C_3H_5)(OCOCF_3)(PMePh_2)_3$	29
3 PMe_3	CH_2=$CHCH_2OCOMe$	$Ru(\eta^3\text{-}C_3H_5)(OCOMe)(PMe_3)_3$	24
3 PMe_3	CH_2=$CHCH_2OCOPh$	$Ru(\eta^3\text{-}C_3H_5)(OCOPh)(PMe_3)_3$	12
3 PMe_3	$MeCH$=$CHCH_2OCOCF_3$	$Ru(\eta^3\text{-}C_4H_7)(OCOCF_3)(PMe_3)_3$	39
3 PMe_3	CH_2=$CHCH(Me)OCOCF_3$	$Ru(\eta^3\text{-}C_4H_7)(OCOCF_3)(PMe_3)_3$	55
3 PMe_3	$PhCH$=$CHCH_2OCOCF_3$	$Ru(\eta^3\text{-}C_4H_7)(OCOCF_3)(PMe_3)_3$	25
3 PMe_3	CH_2=$CHCH_2OPh$	$Ru(\eta^3\text{-}C_3H_5)(OPh)(PMe_3)_3$	37
3 PMe_3	CH_2=$CHCH_2O(C_6H_4Me\text{-}2)$	$Ru(\eta^3\text{–}C_3H_5)(OC_6H_4Me\text{-}2)(PMe_3)_3$	30
3 PMe_3	CH_2=$CHCH_2O(C_6H_4Et\text{-}2)$	$Ru(\eta^3\text{-}C_3H_5)(OC_6H_4Et\text{-}2)(PMe_3)_3$	10
3 PMe_3	CH_2=$CHCH_2O(C_6H_4OMe\text{-}2)$	$Ru(\eta^3\text{–}C_3H_5)(OC_6H_4OMe\text{-}2)(PMe_3)_3$	15
2 DEPE	CH_2=$CHCH_2SPh$	$[Ru(\eta^3\text{-}C_3H_5)(DEPE)_2](SPh)$	90
2 DEPE	CH_2=$CHCH_2SMe$	$[Ru(\eta^3\text{-}C_3H_5)(DEPE)_2](SMe)$	5
2 DEPE	CH_2=$CHCH_2OPh$	$[Ru(\eta^3\text{-}C_3H_5)(DEPE)_2](OPh)$	90
2 DEPE	CH_2=$CHCH_2OCOCF_3$	$[Ru(\eta^3\text{-}C_3H_5)(DEPE)_2](OCOCF_3)$	80
2 DEPE	CH_2=$CHCH_2OCOMe$	$[Ru(\eta^3\text{-}C_3H_5)(DEPE)_2](OCOMe)$	75

Table 3 Coefficients for C^2 and C^5 in the LUMO of substituted thiophene, calculated by PM3

Thiophene	C^2	C^5
	−0.62	−0.40
	−0.63	−0.41



Scheme 11

whereas reaction of the zero-valent iron fragment "Fe(DEPE)$_2$", derived from $Fe(N_2)(DEPE)_2$ led to competitive C–S and C–H bond cleavage reactions,[46,47] the ruthenium complex exclusively cleaved the C–S bond of acetyl or formyl substituted thiophene.

Of particular interest is that ruthenium exclusively favours the cleavage of the C(2)–S bond for 3-acetyl substituted thiophene and C(5)–S bond for 2-acetyl substituted thiophene. The PM3 calculations indicated that 3-acetyl- and 3-formylthiophenes have large LUMO coefficients at their C(2) carbon, due to effective back donation from electron-rich ruthenium (Table 3).[45]

Thus, 3-substituted thiophenes are considered to give rise to selective cleavage at the C(2)–S bond. On the other hand, the observed C(5)–S selectivity for 2-substituted thiophenes is likely to arise from steric repulsion between the ruthenium moiety and the substituent at the 2-position, preventing close approach to the ruthenium centre.

3.4. Carbon–hydrogen and nitrogen–hydrogen bond cleavage of heterocyclic compounds

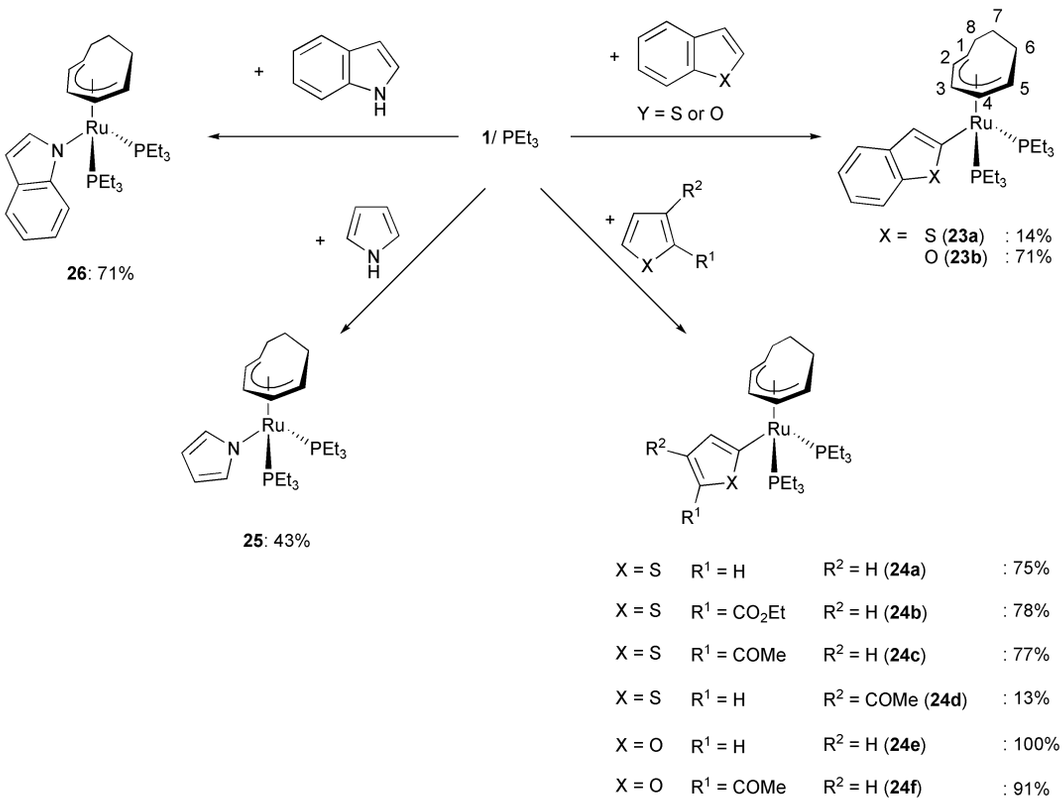
Although insertion of ruthenium into the C–S bond of thiophene took place in the presence of DEPE, reactions of **1** with thiophenes in the presence of PEt_3 exclusively cleaved the C–H bond at the 2- (or 5-)position to give (η^5-cyclo-octadienyl)-(thienyl)bis(triethylphosphine)ruthenium(II) as shown in Scheme 12.[48] Other regioselective C–H or N–H bond cleavage reactions of various heterocyclic compounds such as benzothiophene, furan, benzofuran, pyrrole and indole also gave analogous complexes (Scheme 12).

These reactions are regarded as formal protonation of the 1,3,5-COT ligand by these heterocyclic compounds. Detailed analysis of the reaction revealed that the reaction of **1** with benzothiophene proceeded *via* **1**, **2b**, **4c** and finally **23a**. When the isolated **4c** was employed as a starting complex in this reaction, the rate became much faster than that of the **1**/PEt_3 system. Therefore, complex **4c** is considered as an intermediate complex in this reaction. The kinetic study of the reaction of **4c** with benzothiophene indicated that the reaction is first-order for [**4c**] and [benzothiophene] and the reciprocal of the initial rate was proportional to [PEt_3], suggesting the prerequisite prior dissociation of a PEt_3 from **4c** to give a co-ordinatively unsaturated species for these reactions. It is worth noting that Jones[49] and Sargent[50] experimentally and theoretically showed that C–H bond cleavage of thiophene by isoelectronic Rh(I) complex takes place *via* prior η^2-C=C intermediate, whereas the C–S bond cleavage is followed by prior η^1-S co-ordination. Since the present system exclusively gives C–H bond cleavage products of benzothiophene *via* a ruthenium(0) intermediate **B** (Scheme 13), this process may also have proceeded *via* the η^2-C=C intermediate **C** (Scheme 13).

4. sp^3 Carbon–hydrogen bond cleavage by use of a chalcogen anchor

4.1. sp^3 Carbon–hydrogen bond cleavage of *ortho*-substituents in phenols

Among carbon–hydrogen bond cleavage reactions, it is generally accepted that sp^3 C–H bond cleavage is the most difficult task because of both kinetic and thermodynamic reasons.[51] In fact, less examples of the sp^3 C–H bond cleavage reaction are documented in comparison with those of the sp^2 C–H bond cleavage reactions.[51,52] However, if the sp^3 C–H bond is placed very close to the ruthenium centre, facile bond cleavage is expected to take place (Chart 1).



Scheme 12

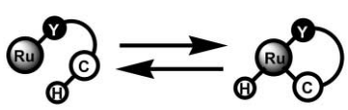
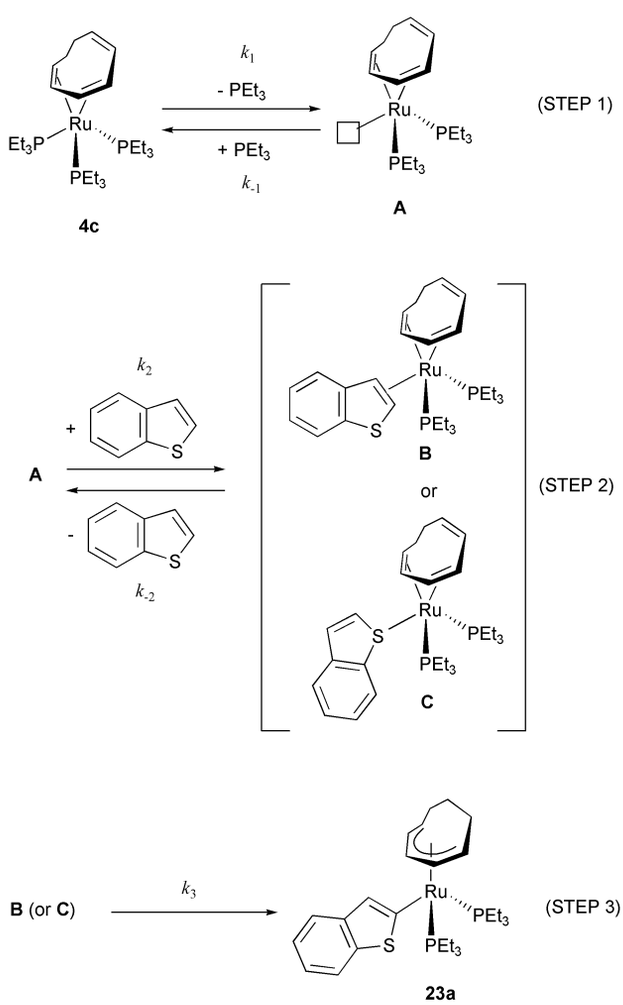


Chart 1

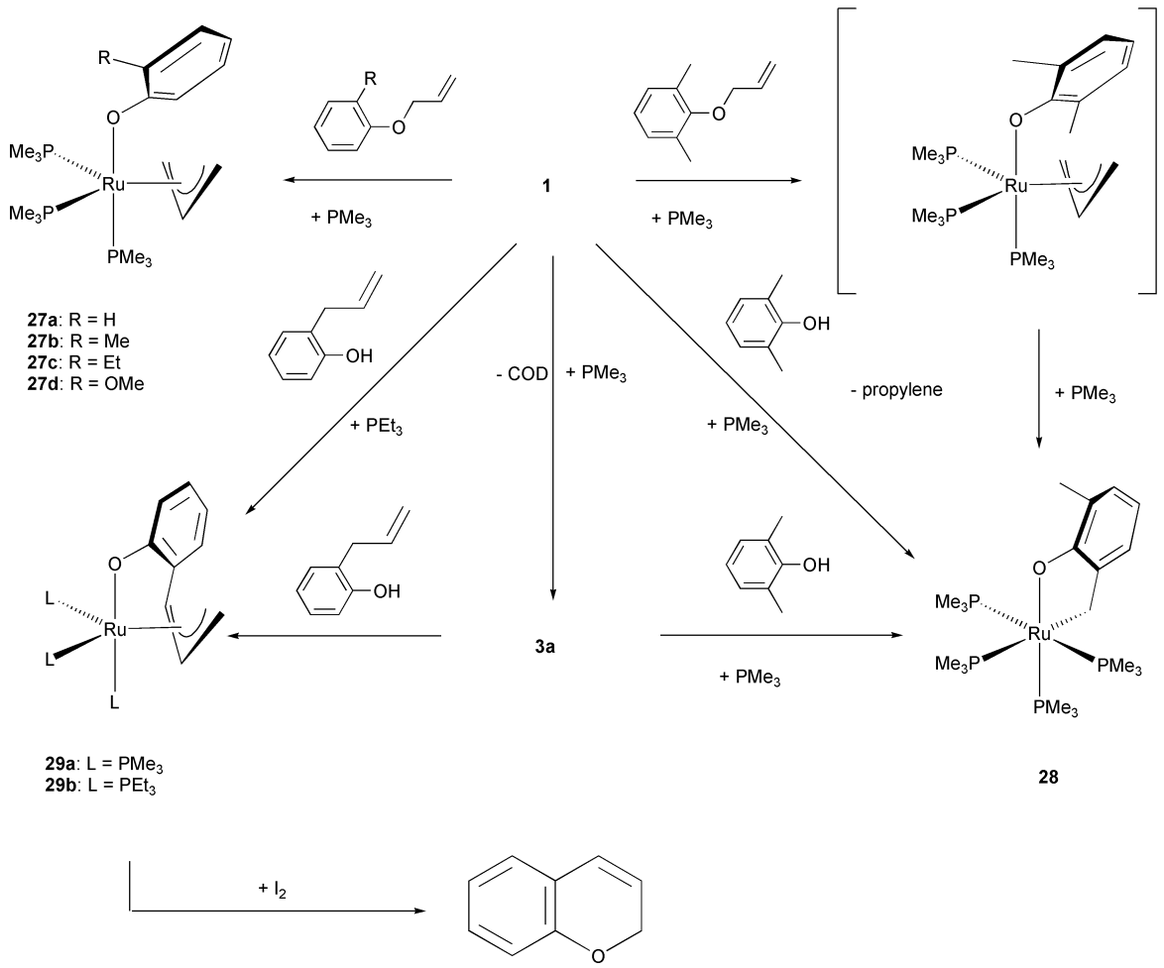
In fact, although reaction of **1**/PMe_3 with allyl phenyl ether or allyl *ortho*-mono-substituted phenyl ether only gave (η^3-allyl)(aryloxo)ruthenium(II) complexes *via* C–O bond oxidative addition as shown in Section 3.2, treatment with allyl 2,6-xylyl ether led to the formation of an oxaruthenacycle complex **28** (Scheme 14).[53]

Since oxidative addition of allyl aryl ether is known and the evolution of propylene was observed in the reaction, complex **28** is considered to be formed *via* the (η^3-allyl)(aryloxo)-ruthenium(II). This reaction may involve oxidative addition of the sp^3 C–H bond of the *ortho*-methyl group, followed by reductive elimination of the hydrido and the allyl ligands, or direct hydrogen abstraction by the allyl moiety. Similar reaction also takes place for 2,6-xylenol and 2-allylphenol as shown in Scheme 14. The following mechanism has been proposed from detailed analyses of the reaction of **1**/PMe_3 with phenol derivatives. Treatment of **1**/PMe_3 with phenols rapidly resulted in the protonation of the 1,3,5-COT ligand giving a cationic (η^5-cyclo-octadienyl)ruthenium(II) complex, **30** (Scheme 15).[54]

Chaudret and co-workers also reported protonation of **1** with HBF_4,[55] where the proton attacks at the ruthenium centre followed by migration of the hydride to the 1,3,5-COT ligand to give (η^5-cyclo-octadienyl)ruthenium(II). Complex **30** would also be formed by a similar mechanism. Heating of **30** in the presence of PMe_3 produced an oxaruthenacycle complex **28**. Similar treatment of **1**/PMe_3 with 2-allylphenol gave an oxa-ruthenacycle complex **29**, but that with phenol or 2-cresol gave *cis*-(aryloxo)(hydrido)ruthenium(II) complex **31**.[54] 2,6-Disubstitution may provide effective orbital overlap between the C–H bond and the ruthenium centre and the C–H bond in the 2-allyl group may be more susceptible to cleavage in general.



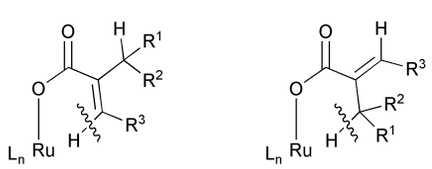
Scheme 13



Scheme 14

4.2. Preferential sp^3 C–H over sp^2 C–H bond cleavage in α-alkyl-α,β-unsaturated carboxylic acids

Reactions of **1** with α,β-unsaturated carboxylic acids such as acrylic acid and methacrylic acid were studied. If α-alkyl-α,β-unsaturated carboxylic acids protonate the 1,3,5-COT ligand in **1** in the presence of PMe_3 as shown for HBF_4,[55] HPF_6[56] and several carboxylic acids,[57] two possible interactions of sp^2 and sp^3 C–H bonds with ruthenium in a putative carboxylatoruthenium(II) intermediate are considered as shown in Chart 2.



sp^2 C-H bond cleavage *sp^3 C-H bond cleavage*

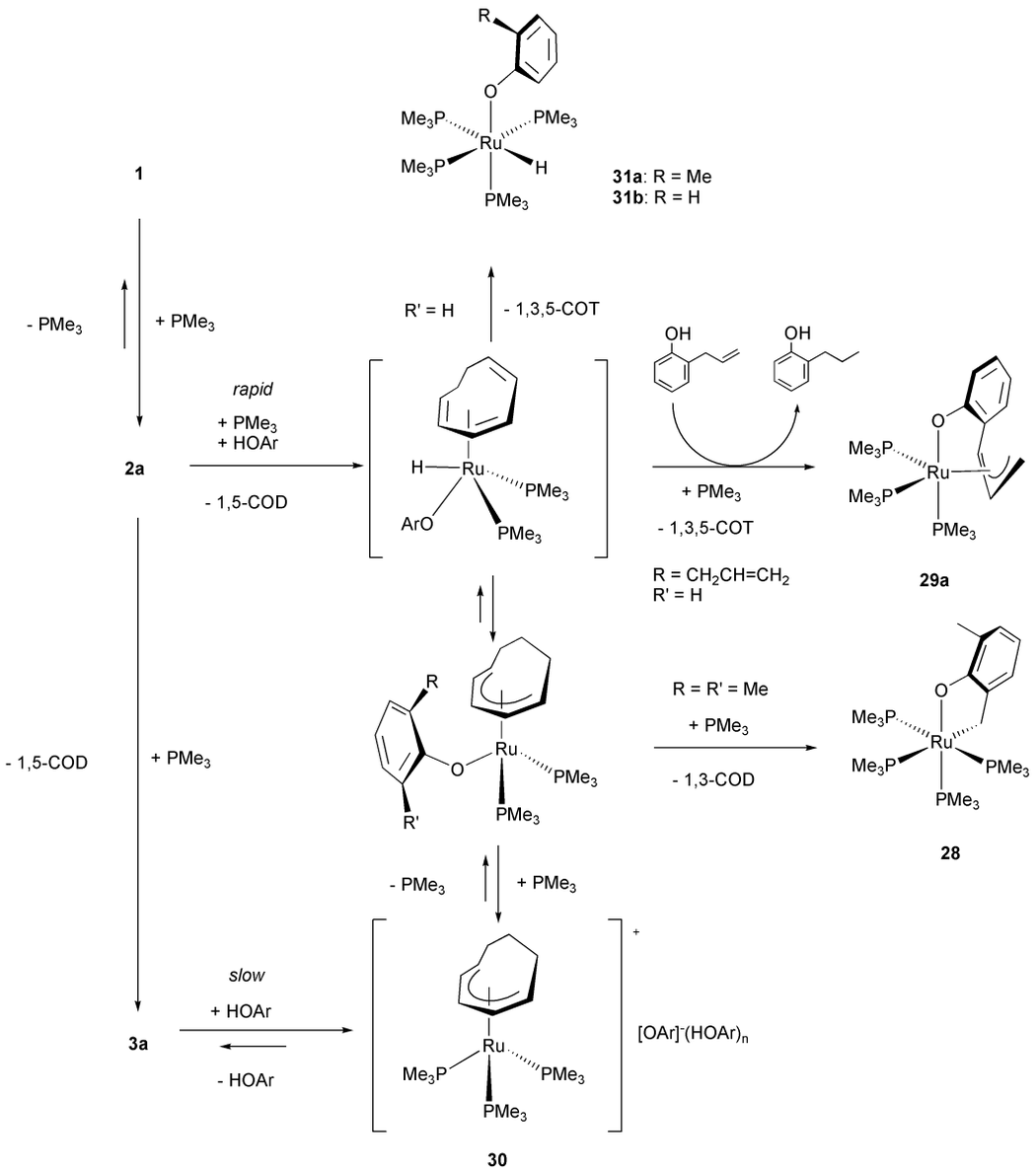
Chart 2

Therefore, this system could provide a good probe for discriminating between the competitive sp^3 C–H and sp^2 C–H bond cleavage reactions at ruthenium(II). Actually, treatment of **1**/PMe_3 with α,β-unsaturated acid initially afforded bis(carboxylato)ruthenium(II) complex **32** with liberation of 1,3- and 1,5-COD. Then, the reaction was followed by slow formation of five-membered ruthenalactone complexes *via* C–H bond activation (Scheme 16).[58]

The selectivity of the bond cleavage reaction was examined by use of labeled methacrylic acid, $^{13}CH_2$=$CMeCO_2H$, showing exclusive bond activation at the β-methylene C–H bond. Similarly, a series of α-alkyl acrylic acids such as methacrylic acid, α-ethyl acrylic acid, α-propyl acrylic acid, and α-isopropyl acrylic acid were found to react with **1**/PMe_3 at the β-carbon, suggesting that sp^2 C–H bond activation is a highly preferred process compared to sp^3 C–H bond cleavage. In spite of these facts, the reaction of **1**/PMe_3 with tiglic acid and α-methyl cinnamic acid preferentially afforded ruthenalactone products **33b** or **33e**, which were considered to be formed by preferential sp^3 C–H bond cleavage followed by a 1,3-hydrogen shift over the sp^2 C–H bond. Detailed analysis of the reaction monitored by NMR indicates prior formation of six-co-ordinate bis(carboxylato)ruthenium(II) complex which is not retarded by added PMe_3. σ-Bond metathesis of the less hindered methyl C–H with the carboxylato O–Ru bond to form a five-membered ruthenalactone could be a possible mechanism, though mechanistic details are not clear so far. Nevertheless, the present results clearly show that the sp^3 C–H can be favoured over the sp^2 C–H bond in the bond cleavage reaction at ruthenium(II) when the sp^2 carbon has a substitutent.

5. Oxidative addition of active methylene compounds

The C–H oxidative addition of active methylene compounds has been paid less attention than that of unactivated C–H bonds.[59] As described before, activated methylene compounds are also expected to behave like other Brϕnsted acids, since their C–H bonds are acidic. Especially the reactions of cyanoesters and 1,3-dicarbonyl compounds with **1**/L are described in relation to the highly chemoselective catalytic Knöevenagel and Michael reactions.



Scheme 15

5.1. Enolatoruthenium(II) complexes from cyanoesters

When ethyl cyanoacetate was treated with **1** in the presence of tertiary phosphines such as PPh_3, PMe_2Ph and DPPE, formal oxidative addition took place to give zwitterionic cyano-bonded enolatoruthenium(II) complexes as shown in Scheme 17.[60]

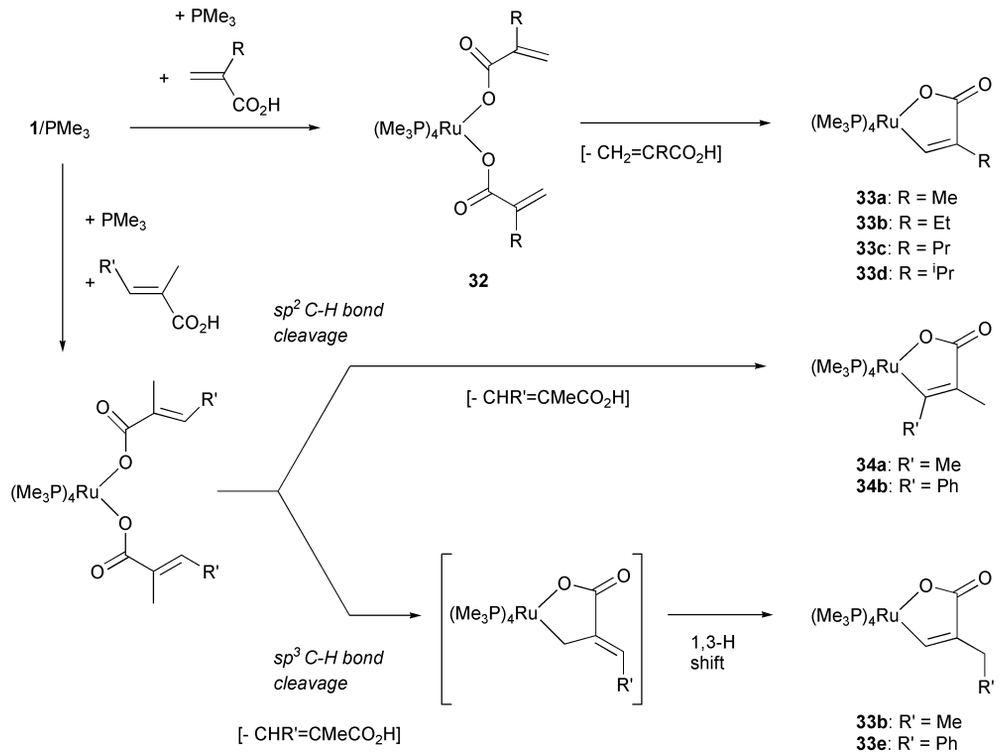
Exclusive binding *via* the cyano group forces the enolato ligand zwitterionic rather than normal *O*- and *C*-bonded enolato co-ordination modes. The PPh_3 complex **36** has an intermolecular hydrogen bonding of the enolato ligand with one cyanoester to stabilise the *cis* enolate co-ordination,[61,62] while *trans* configuration is observed for other cases. When DPPE was used as a ligand, an intermediate complex **38** was isolated.[60] Because of this zwitterionic structure of these enolato ligands, their nucleophilicity increases extensively to react with electrophiles such as methyl iodide, benzaldehyde and so on to result in clean C–C bond formation.

When dideuterated ethyl cyanoacetate, $NCCD_2CO_2Et$ was employed in this reaction, *trans*-RuD($NCCDCO_2Et$-κ^1N)-$(DPPE)_2$ (**39a**-d_2) was formed. This fact indicates that the hydride ligand originates from the α-methylene protons of ethyl cyanoacetate, showing that formal oxidative addition of the C–H (or C–D) bond was taking place to ruthenium(0). Though Chaudret and co-workers reported scrambling between ruthenium-hydride and protons among cyclopolyenes in [RuH-(1,5-COD)(1,3,5-COT)][BF_4],[55] such a process is not observed in our system. All these zwitterionic enolatoruthenium(II) complexes showed high catalytic activity toward the Knöevenagel reaction, and the representative results of catalytic reactions are shown in Table 4.

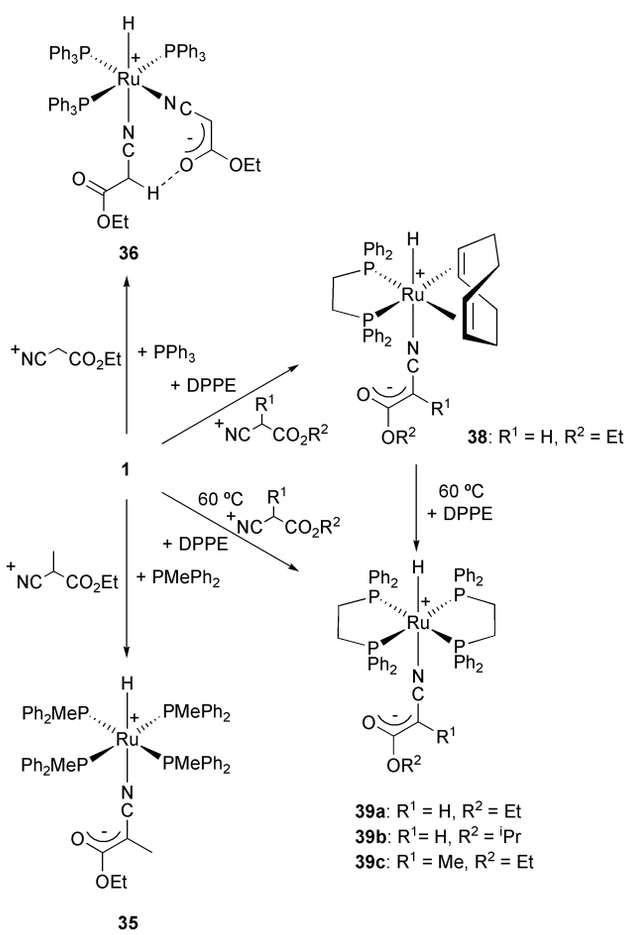
It is interesting to note that complex **39a** shows much higher activity than **36** for the catalytic Knöevenagel reaction. The higher catalytic activity of **39** than **36** toward electrophiles may be due to (i) the absence of intramolecular hydrogen bonding between the enolato and the ester moieties shown in **36**, and (ii) the presence of four phosphorus donors making the enolato ligand more nucleophilic.

Complex **39a** is also active catalyst for the Michael reaction.[63] Complex **39a** reacted with Michael acceptors such as methyl acrylate giving the new enolatoruthenium(II) complex (mono-Michael adduct complex), *trans*-RuH[$NCC(C_2H_4CO_2Me)$-CO_2Et-κ^1N]$(DEPE)_2$ (**40**). Single crystals of **39a** and **40** were obtained and the molecular structures are depicted in Fig. 3.[64]

The molecular structure of **39a** unambiguously shows the enolate ligand co-ordinating to the ruthenium *via* nitrogen and the hydrido and enolato ligands being mutually *trans*. The mono-Michael adduct **40** is considered to be formed by the direct reaction of the enolato ligand to the methyl acrylate followed by a 1,3-hydrogen shift. Interestingly, they did not react at all with active methylene compounds or Michael acceptors,

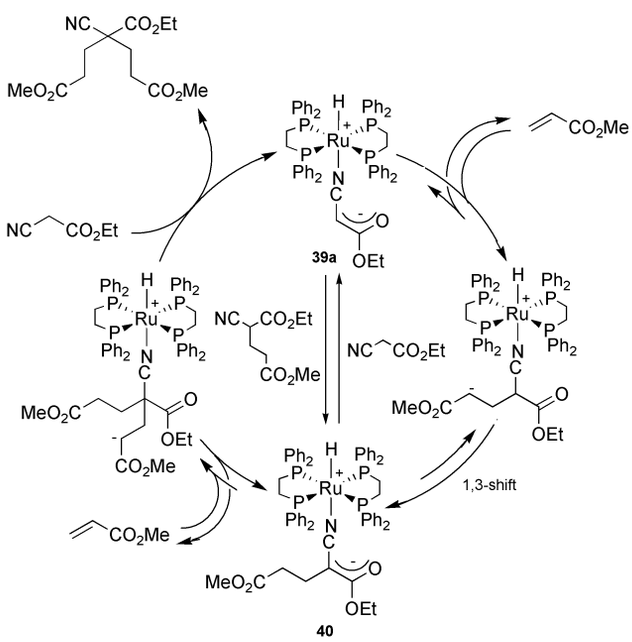


Scheme 16



Scheme 17

but the presence of both reagents led to the formation of Michael products. Thus, catalytic Michael reactions were smoothly promoted by complexes **39a** and **40** as illustrated in Scheme 18, where the final Michael product would be released *via* protonation by Michael acceptor.[63]



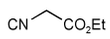
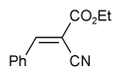
Scheme 18

5.2. Enolatoruthenium(II) complexes derived from 1,3-dicarbonyl compounds

1,3-Dicarbonyl compounds such as 2,4-pentanedione also gave enolatoruthenium(II) complexes, in which the normal *O*,*O*′-chelating co-ordination mode was observed. These complexes showed no reactivity toward electrophiles such as methyl iodide and benzaldehyde, giving rise to no catalytic activity. This contrasting difference in chemical reactivity of the enolato ligands (zwitterionic and *O*,*O*′-chelate) is the reason why the completely chemoselective Ru-catalysed catalytic Knöevenagel and Michael reactions (Murahashi reaction) were accomplished, where the cyanoacetate exclusively reacted even when a mixture of ethyl cyanoacetate and 2,4-pentanedione with the same pK_a value was used as starting nucleophile.[65]

In order to increase the nucleophilicity of the enolato ligand

Table 4 Catalytic Knöevenagel reaction between ethyl cyanoacetate and benzaldehyde

Catalyst	Active hydrogen compound	Electrophile	Product	Yield (%)
DPPE		PhCHO		0.8
1				29
1 + DPPE				32
36				29
38				52
39a				76
39b				80

Conditions: catalyst = 1.0 mol%, solvent = THF, 50 °C, 36 h.

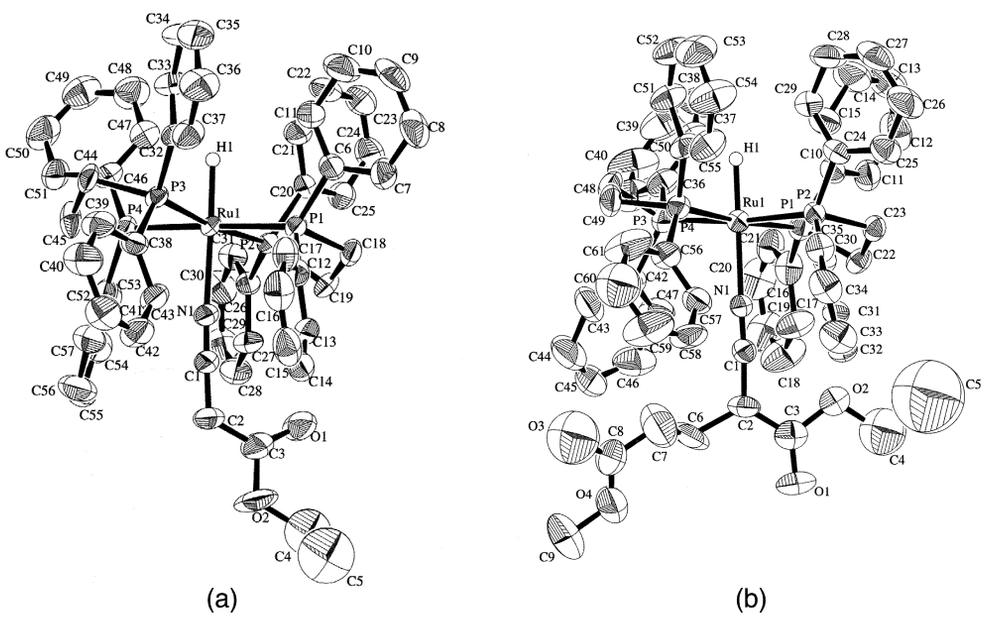
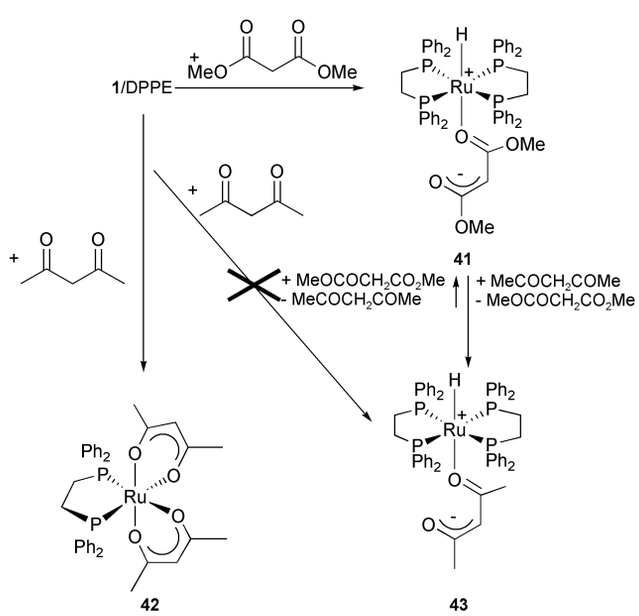


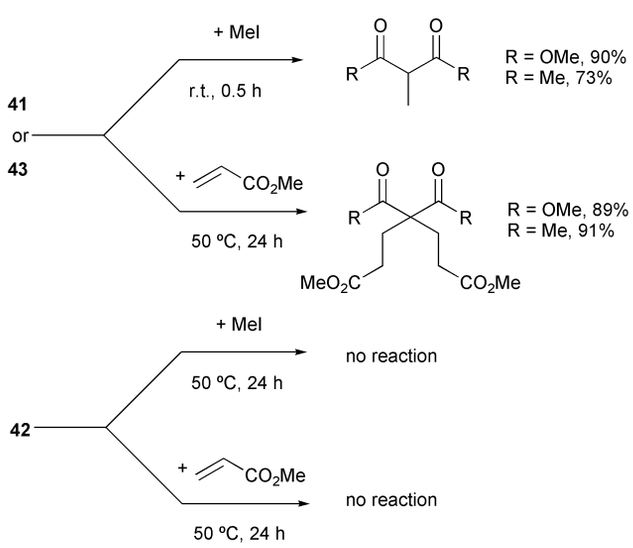
Fig. 3 Molecular structures of (a) *trans*-RuH(NCCHCO$_2$Et-κ^1*N*)(DPPE)$_2$ (**39a**) and (b) the mono-Michael adduct complex of methyl acrylate, *trans*-RuH[NCC(C$_2$H$_4$CO$_2$Me)CO$_2$Et-κ^1*N*](DPPE)$_2$ (**40**).

derived 1,3-dicarbonyl compounds, bidentate phosphine ligands were used to cause the linkage isomerism of the enolato ligand giving monodentate co-ordination. In fact, when dimethyl malonate was treated with **1** in the presence of DPPE, *trans*-(hydrido)(dimethyl malonato-κ^1*O*)ruthenium(II) was obtained (Scheme 19).[66,67]



Scheme 19

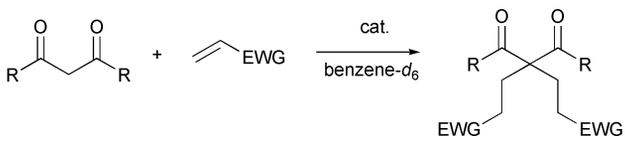
Enolato exchange of this complex by 2,4-pentanedione also gave a κ^1-*O*-2,4-pentanedionato analogue. As expected, the nucleophilicity of the enolato ligand significantly increased to react with the Michael acceptors (Scheme 20).



Scheme 20

Although κ^1*O*-enolato ligand is considered as a simple alkoxo type ligand, the canonical zwitterionic structure can also be considered. The high reactivity of these complexes towards

Table 5 Catalytic Michael reaction of 1,3-dicarbonyls with acceptors

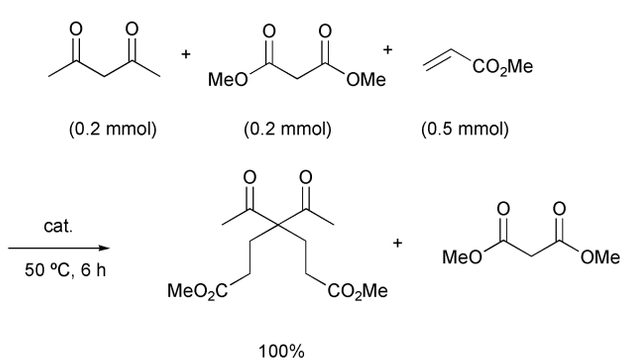


Catalyst	R	EWG	Temperature/°C	Time/h	Yield (%)
41	OMe	CO_2Me	50	48	89
41	Me	CN	50	96	70
41	OMe	CN	25	48	24
41	Me	CO_2Me	70	96	60
42	Me	CN	50	48	0
42	Me	CO_2Me	50	48	0
43	Me	CO_2Me	70	96	62

Conditions: catalyst (0.010 mmol), Michael donor (1.0 mmol), and Michael acceptor (2.5 mmol), solvent = benzene, yield based on Michael donor.

Michael acceptors may be due to the significant contribution of the zwitterionic structure. Representative results of catalytic Michael reactions are shown in Table 5.

Moreover, an interesting feature of the κ^1O-enolate complex is the chemoselectivity in catalysis observed in the presence of two different 1,3-dicarbonyl compounds. For example, complex **41** catalyses the Michael reaction of 2.5 equiv. of methyl acrylate with an equimolar mixture of dimethyl malonate ($pK_a = 13$) and 2,4-pentanedione ($pK_a = 9$) giving exclusively the Michael product of 2,4-pentanedione, while a conventional base catalyst such as NaOMe (20 mol%) in THF or PEt_3 in benzene gave a mixture of Michael products of 1,3-dicarbonyls (Scheme 21).



Scheme 21

This chemoselectivity may be explained by the exclusive formation of **43** and the high nucleophilicity of the resulting enolatoruthenium(II) complex **43** derived from 2,5-pentanedione.

6. Concluding remarks

In the present Perspective, we have described formation of zero-valent active species susceptible to the bond cleavage reactions of C–O, C–S, N–H, O–H, and C–H bonds in esters, ethers, sulfide, heterocyclic compounds, phenols and carboxylic acids as well as catalytic Knöevenagel and Michael reactions of active hydrogen compounds. These bond cleavage reactions are no more than elemental reactions as inlets toward organic synthesis but they would provide fundamental concepts closely connected to the non-halogen and zero-emission molecular transformation processes.

7. Acknowledgements

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8. References and notes

1 Abbreviations used in this article: 1,5-COD = 1,5-cyclo-octadiene (C_8H_{12}); 1,3,5-COT = 1,3,5-cyclo-octatriene (C_8H_{10}); DPPM = bis-(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$); DMPE = 1,2-bis-(dimethylphenylphosphino)ethane ($Me_2PC_2H_4PMe_2$); DEPE = 1,2-bis(diethylphosphino)ethane ($Et_2PC_2H_4PEt_2$); TRIPHOS = bis(di-phenylphosphinoethyl)phenylphosphine ($Ph_2PC_2H_4PPhC_2H_4PPh_2$).
2 E. O. Fischer and J. Müller, *Chem. Ber.*, 1963, **96**, 3217.
3 (*a*) P. Pertici, G. Vitulli and L. Porri, *J. Chem. Soc., Chem. Commun.*, 1975, 846; (*b*) P. Pertici, G. Vitulli, M. Paci and L. Porri, *J. Chem. Soc., Dalton Trans.*, 1980, 1961.
4 K. Itoh, H. Nagashima, T. Ohshima, N. Oshima and H. Nishiyama, *J. Organomet. Chem.*, 1984, **272**, 179.
5 K.-M. Frosin and L. Dahlenburg, *Inorg. Chim. Acta*, 1990, **167**, 83.
6 M. A. Bennett, in *Comprehensive Organometallic Chemistry II*, E. W. Abel, F. G. A. Stone, G. Willkinson and M. I. Bruce, eds., Oxford, 1995, vol. 7, p. 549.
7 T. Mitsudo, Y. Hori and Y. Watanabe, *J. Organomet. Chem.*, 1987, **334**, 157.
8 P. Pertici and G. Vitulli, *Comments Inorg. Chem.*, 1991, **11**, 175.
9 Typical catalytic properties of **1** are as follows: (*a*) T. Mitsudo, K. Kokuryo, T. Shinsugi, Y. Nakagawa, Y. Watanabe and Y. Takegami, *J. Org. Chem.*, 1979, **44**, 4492; (*b*) M. Airoldi, G. Deganello, G. Dia and G. Gennaro, *J. Organomet. Chem.*, 1980, **187**, 391; (*c*) M. Airoldi, G. Deganello, G. Dia and G. Gennaro, *Inorg. Chim. Acta*, 1983, **68**, 179; (*d*) T. Mitsudo, Y. Nakagawa, K. Watanabe, Y. Hori, H. Misawa, H. Watanabe and Y. Watanabe, *J. Org. Chem.*, 1985, **50**, 565; (*e*) T. Mitsudo, S.-W. Zhang, M. Nagao and Y. Watanabe, *J. Chem. Soc., Chem. Commun.*, 1991, 598; (*f*) Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh and J. Y. Satoh, *J. Am. Chem. Soc.*, 1991, **113**, 9604; (*g*) T. Mitsudo, S.-W. Zhang, N. Satake, T. Kondo and Y. Watanabe, *Tetrahedron Lett.*, 1992, **33**, 5533; (*h*) S.-W. Zhang, T. Mitsudo, T. Kondo and Y. Watanabe, *J. Organomet. Chem.*, 1993, **450**, 197; (*i*) Y. Maruyama, T. Sezaki, M. Tekawa, T. Sakamoto, I. Shimizu and A. Yamamoto, *J. Organomet. Chem.*, 1994, **473**, 257; (*j*) T. Mitsudo, S.-W. Zhang and Y. Watanabe, *J. Chem. Soc., Chem. Commun.*, 1994, 435; (*k*) T. Mitudo, N. Suzuki, T. Kondo and Y. Watanabe, *J. Org. Chem.*, 1994, **59**, 7759; (*l*) S.-W. Zhang, T. Mitsudo, T. Kondo and Y. Watanabe, *J. Organomet. Chem.*, 1995, **485**, 55; (*m*) A. Fukuoka, T. Nagano, S. Furuta, M. Yoshizawa, M. Hirano and S. Komiya, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1409; (*n*) T. Mitsudo, T. Suzuki, S.-W. Zhang, D. Imai, K. Fujita, T. Manabe, M. Shiotsuki, Y. Watanabe, K. Wada and T. Kondo, *J. Am. Chem. Soc.*, 1999, **121**, 1839; (*o*) T. Sato, N. Komine, M. Hirano and S. Komiya, *Chem. Lett.*, 1999, 441.

10 B. Chaudret, G. Commenges and R. Poilblanc, *J. Chem. Soc., Chem. Commun.*, 1982, 1388.
11 P. Pertici, G. Vitulli, W. Porzio, M. Zocchi, P. L. Barili and G. Deganello, *J. Chem. Soc., Dalton Trans.*, 1983, 1553.
12 B. Chaudret, G. Commenges and R. Poilblanc, *J. Chem. Soc., Dalton Trans.*, 1984, 1635.
13 K. Itoh, K. Mukai, H. Nagashima and H. Nishiyama, *Chem. Lett.*, 1983, 499.
14 G. Deganello, A. Mantovani, P. L. Sandrini, P. Pertici and G. Vitulli, *J. Organomet. Chem.*, 1977, **135**, 215.
15 (*a*) P. Pertici, G. P. Simonelli, G. Vitulli, G. Deganello, P. L. Sandrini and A. Mantovani, *J. Chem. Soc., Chem. Commun.*, 1977, 132; (*b*) P. Pertici, G. Vitulli, C. Carlini and F. Ciardelli, *J. Mol. Catal.*, 1981, **11**, 353; (*c*) P. Pertici, G. Vitulli, R. Lazzaroni, P. Salvadori and P. L. Barili, *J. Chem. Soc., Dalton Trans.*, 1982, 1019; (*d*) P. Pertici, G. Vitulli, C. Bigelli and R. Lazzaroni, *J. Organomet. Chem.*, 1984, **275**, 113; (*e*) M. Hirano, T. Shibasaki, S. Komiya and M. A. Bennett, *Organometallics*, 2002, **21**, 5738.
16 P. Pertici, G. Vitulli, W. Porzio and M. Zocchi, *Inorg. Chim. Acta Lett.*, 1979, **37**, L521.
17 Cone angles of phosphines employed: PMe_3 (118°), PMe_2Ph (122°), PEt_3 (132°), PBu_3 (132°), PEt_2Ph (136°), PPh_3 (145°), P^iPr_3 (160°), PCy_3 (170°).
18 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
19 M. Hirano, T. Marumo, T. Miyasaka, A. Fukuoka and S. Komiya, *Chem. Lett.*, 1997, 297.
20 J. G. Planas, T. Marumo, Y. Ichikawa, M. Hirano and S. Komiya, *J. Mol. Catal.*, 1999, **147**, 137.
21 S. Komiya, J. G. Planas, K. Onuki, Z. Lu and M. Hirano, *Organometallics*, 2000, **19**, 4051.
22 G. Alibrandi and B. E. Mann, *J. Chem. Soc., Dalton Trans.*, 1992, 1439.
23 M. Grassi, B. E. Mann, P. Manning and C. M. Spencer, *J. Organomet. Chem.*, 1986, **307**, C55.
24 M. Hirano, C. Nagata and S. Komiya, unpublished work.
25 M. A. Bennett, T. W. Matheson, G. B. Robertson, A. K. Smith and P. A. Tucker, *Inorg. Chem.*, 1980, **19**, 1014.
26 F. A. Cotton and R. Eiss, *J. Am. Chem. Soc.*, 1969, **91**, 6593.
27 (*a*) A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, *J. Am. Chem. Soc.*, 1952, **74**, 4867; (*b*) W. Adam and I. Erden, *Tetrahedron Lett.*, 1979, **30**, 2781; (*c*) W. Adam, N. Gretzke, L. Hasemann, G. Klug, E.-M. Peters, K. Peters, H. G. von Schnering and B. Will, *Chem. Ber.*, 1985, **118**, 3357.
28 A similar reaction and mechanism was also reported for the $M(CO)_3$ (M = Fe, Ru) fragment: (*a*) A. J. P. Domingos, B. F. G. Johnson and J. Lewis, *J. Organomet. Chem.*, 1973, **49**, C33; (*b*) A. J. P. Domingos, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1975, 2288; (*c*) A. Nakamura and N. Hagihara, *Nippon Kagaku Zasshi*, 1961, **82**, 1389.
29 The ring slippage of 1,3,5-COT by Lewis bases cannot be ruled out: L. J. Farrugia, J. C. Jeffery, C. Marsden and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 645.
30 S. Komiya, M. Ito and M. Hirano, unpublished work.
31 Ch. Elschenbroich and A. Salzer, *Organometallics. A Concise Introduction*, 2nd revised edn., VCH, Weinheim, 1992, p. 230.
32 G. Pacchioni and P. S. Bagus, *Inorg. Chem.*, 1992, **31**, 4391.
33 M. Hirano, R. Asakawa, C. Nagata, T. Miyasaka, N. Komine and S. Komiya, submitted for publication.
34 An alternative method for the synthesis of **9j** was reported with spectroscopic characterisation: M. A. Bennett, Z. Lu, X. Wang, M. Bown and D. C. R. Hockless, *J. Am. Chem. Soc.*, 1998, **120**, 10409.
35 An alternative method for the preparation of **12** was reported: J.-M. Bassett, D. E. Berry, G. K. Barker, M. Green, J. A. K. Howard and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1979, 1003.
36 An alternative method for the preparation of **13** was reported: (*a*) M. Preece, S. D. Roinson and J. N. Wingfield, *J. Chem. Soc., Dalton Trans.*, 1976, 613; (*b*) C. A. Tolman, A. D. English, S. D. Ittel and J. P. Jesson, *Inorg. Chem.*, 1978, **17**, 2374.
37 (*a*) A. Yamamoto, *Adv. Organomet. Chem.*, 1992, **34**, 111; (*b*) Y.-S. Lin and A. Yamamoto, *Activation of C–O Bonds: Stoichiometric and Catalytic Reactions*, in *Topics in Organometallic Chemistry, Activation of Unreactive Bonds and Organic Synthesis*, S. Murai ed., Springer, Heidelberg, 1999, vol. 3, p. 161; (*c*) S. Komiya and M. Hirano, *Activation f Substrates with Polar Single Bonds*, in *Fundamentals of Molecular Catalysis*, A. Yamamoto and H. Kurosawa, eds., Elsevier, New York, 2003, in press.
38 S. Komiya, J. Suzuki, K. Miki and N. Kasai, *Chem. Lett.*, 1987, 1287.
39 J. G. Planas, T. Marumo, Y. Ichikawa, M. Hirano and S. Komiya, *J. Chem. Soc., Dalton Trans.*, 2000, 2613.
40 M. Hirano, T. Kobori and S. Komiya, unpublished work.
41 R. A. Jones, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 1771.
42 S. Komiya, T. Kabasawa, K. Yamashita, M. Hirano and A. Fukuoka, *J. Organomet. Chem.*, 1994, **471**, C6.42.
43 J. G. Planas, M. Hirano and S. Komiya, *Chem. Lett.*, 1998, 123.
44 R. A. Sanchez-Delgado, *Organometallic Modeling of the Hydrodesulfurization and Hydrodenitrogenation Reactions*, Kluwer Academic, Dordrecht, 2002.
45 J. G. Planas, M. Hirano and S. Komiya, *Chem. Commun.*, 1999, 1793.
46 T. Morikita, M. Hirano, A. Sasaki and S. Komiya, *Inorg. Chim. Acta*, 1999, **291**, 341.
47 M. Hirano, M. Akita, T. Morikita, H. Kubo, A. Fukuoka and S. Komiya, *J. Chem. Soc., Dalton Trans.*, 1997, 3453.
48 M. Hirano, K. Onuki, Y. Kimura and S. Komiya, *Inorg. Chim. Acta*, in press.
49 (*a*) W. D. Jones and L. Dong, *J. Am. Chem. Soc.*, 1991, **113**, 559; (*b*) A. L. Sargent, S. B. Duckett, K. F. Ohman and W. D. Jones, *J. Am. Chem. Soc.*, 1992, **114**, 151.
50 L. A. Sargent and E. P. Titus, *Organometallics*, 1998, **17**, 65.
51 B. A. Arndtsen, R. G. Bergman, T. A. Mobley and T. H. Peterson, *Acc. Chem. Res.*, 1995, **28**, 154.
52 (*a*) A. E. Shilov, *The Activation of Saturated Hydrocarbons by Transition Metal Complexes*, Reidel, Dordrecht, 1984; (*b*) R. H. Crabtree, *Chem. Rev.*, 1985, **85**, 245; (*c*) E. P. Wasserman, C. B. Moore and R. G. Bergman, *Science*, 1992, **255**, 315; (*d*) W. R. Moser and D. W. Slocum, *Homogeneous Transition Metal Catalyzed Reactions*, *Advances in Chemistry 230*, American Chemical Society, Washington DC, 1992.
53 M. Hirano, N. Kurata, T. Marumo and S. Komiya, *Orgnaometallics*, 1998, **17**, 501.
54 M. Hirano, N. Kurata and S. Komiya, *J. Organomet. Chem.*, 2000, **607**, 18.
55 (*a*) F. Bouachir, B. Chaudret and I. Tkatchenko, *J. Chem. Soc., Chem. Commun.*, 1986, 94; (*b*) F. Bouachir, B. Chaudret, F. Dahan, F. Agbossou and I. Tkatchenko, *Organometallics*, 1991, **10**, 455.
56 G. Vitulli, P. Pertici and C. Bigelli, *Gazz. Chim. Ital.*, 1985, **115**, 79.
57 (*a*) K. Sano, T. Yamamoto and A. Yamamoto, *Z. Naturforsch., Teil B*, 1985, **40**, 210; (*b*) K. Osakada, G. A. Grohmann and A. Yamamoto, *Organometallics*, 1990, **9**, 2092.
58 S. Kanaya, N. Komine, M. Hirano and S. Komiya, *Chem. Lett.*, 2001, 1284.
59 S.-I. Murahashi and H. Takaya, *Acc. Chem. Res.*, 2000, **33**, 225.
60 M. Hirano, A. Takenaka, Y. Mizuho, M. Hiraoka and S. Komiya, *J. Chem. Soc., Dalton Trans.*, 1999, 3209.
61 (*a*) Y. Mizuho, N. Kasuga and S. Komiya, *Chem. Lett.*, 1991, 2127; (*b*) S.-I. Murahashi, T. Naota, H. Taki, M. Mizuno, H. Takaya, S. Komiya, Y. Mizuho, N. Oyasato, M. Hiraoka, M. Hirano and A. Fukuoka, *J. Am. Chem. Soc.*, 1995, **117**, 12436.
62 M. Hirano, M. Hirai, Y. Ito, T. Tsurumaki, A. Baba, A. Fukuoka and S. Komiya, *J. Organomet. Chem.*, 1998, **569**, 3.
63 M. Hirano, S. Kiyota, M. Imoto and S. Komiya, *Chem. Commun.*, 2000, 1679.
64 S. Kiyota, M. Hirano and S. Komiya, unpublished work.
65 R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, 1953, **75**, 2439.
66 S. G. Alvarez, S. Hasegawa, M. Hirano and S. Komiya, *Tetrahedron Lett.*, 1998, **39**, 5209.
67 The molecular structure of the related *trans*-FeH(methyl acetoacetonato-κ^1O)$(DEPE)_2$ and its dynamic behaviour will be published elsewhere: S. Kiyota, J. Tamuki, M. Hirano and S. Komiya, submitted for publication.