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PAPER

Facile η^5–η^3 hapticity interconversion in pentamethylcyclopentadienyl ruthenium(II) complexes containing a phenylmethallyl ("open indenyl") ligand†‡

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The indenyl effect has been introduced to pentadienyl ("open cyclopentadienyl") chemistry by preparation of the phenylmethallyl ("open indenyl") ligand oInd^{Me}. The reaction of its potassium salt K(oInd^{Me}) with $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ afforded the sandwich complex $[(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}oInd^{Me})]$ (**1**), which, upon treatment with PMe_3, CO, and 2,6-dimethylphenyl isocyanide (CN-*o*-Xy), easily underwent η^5–η^3 hapticity interconversion and formed the complexes $[(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-}oInd^{Me})(L)]$ (**2**, L = PMe_3; **3**, L = CO; **4**, L = CN-*o*-Xy). In these complexes, the η^3-bound phenylmethallyl ligand adopts an *anti*-conformation with regard to the relative positions of the phenyl and methyl substituents. For the PMe_3 complex *anti*-**2**, slow conversion to the *syn*-isomer was observed, and this equilibrium reaction was monitored by NMR spectroscopy at 50 °C to determine a first order rate constant of $k_{323\,K} = 6.57 \times 10^{-6}$ ($\pm 0.02 \times 10^{-6}$) s^{-1} and an activation barrier of $\Delta G^\circ = 26.8$ kcal mol^{-1}. DFT calculations afforded a stabilization of *syn*-**2** and *syn*-**3** by $\Delta G_{298} = -1.54$ and -1.74 kcal mol^{-1} over the respective *anti*-isomer.

Introduction

Over the last three decades, pentadienyl ("open cyclopentadienyl") complexes have received considerable attention, in particular because of their stronger binding, *vs.* Cp, to transition metals, as for instance demonstrated by the stability of base-free 14-electron open titanocenes,[1] but nonetheless higher reactivity in comparison with the corresponding cyclopentadienyl complexes.[2] More recently, heteropentadienyl ligands were developed (Fig. 1) that display a rich coordination chemistry and lead to metal complexes with enhanced reactivity, arising from their intriguing ability to switch easily between various possible bonding modes (η^5, η^3 or η^1). Thereby, η^5 to η^3 hapticity interconversion is particularly facile, since the interaction between the metal atom and the C–X π-bond is usually relatively weak, providing the possibility to reversibly open a free coordination site for substrate addition and activation.[3] Pentadienyl ligands are also able to adopt a variety of bonding modes,[2] which also explains their reactivity in alkyne coupling reactions,[4] but in comparison hapticity interconversion generally appears to be less facile.[3]

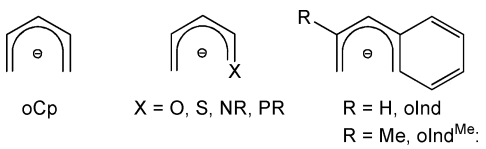

Fig. 1 Pentadienyl (open cyclopentadienyl, oCp), heteropentadienyl and phenylallyl (open indenyl, oInd) ligands.

For Cp complexes, benzannulation represents an alternative method of weakening metal-carbon bonds, and the resulting indenyl complexes often show enhanced ligand substitution rates by providing an associative pathway that involves η^5 to η^3 rearrangement ("indenyl effect").[5] Stabilization of the η^3-indenyl intermediates can be ascribed to partial rearomatization of the unperturbed annulated benzene ring, and this principle should also apply to analogous phenylallyl ligands that can be classified as open indenyl (oInd) ligands (Fig. 1). To the best of our knowledge, however, the indenyl effect has not been adapted to the chemistry of open cyclopentadienyl (oCp) ligands, and, stimulated by our investigation of cycloheptatrienyl-pentadienyl zirconium compexes,[6] we aimed to design more labile pentadienyl ligands by benzannulation. Since 2,4-dimethylpentadienyl (2,4-C_7H_{11}) represents the most widely used pentadienyl ligand in organotransition metal chemistry,[2] we chose to study the coordination chemistry of the open indenyl ligand oInd^{Me} (Fig. 1), in which the methyl substituent should also help to keep this phenylmethallyl ligand in the preferred U-conformation with an *anti*-orientation of the methyl and phenyl groups.[7] In view of the importance of

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† Dedicated to Professor Richard D. Ernst on the occasion of his 60th birthday.

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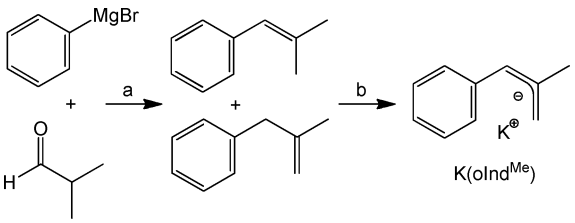
allyl ruthenium species in catalytic allylation and C–C bond formation,[8] the preparation of Ru complexes containing the ligand oInd^{Me} bound in an η^5-fashion were targeted first, and these results, along with studies of potential hapticity interconversions in these systems, are presented in this contribution.

Results and discussion

Ligand synthesis

NMR studies involving the lithium and potassium salts of the phenylmethallyl anion oInd^{Me} have been published previously.[9] Likewise, the reaction of phenyl magnesium bromide with isobutyraldehyde afforded a mixture of phenyl-2-methylpropenes on a multigram scale from inexpensive, commercially available starting-materials (Scheme 1).[9b] In our hands, this isobutene mixture was readily deprotonated by adopting the general procedure for the preparation of pentadienyl anions,[10] and 2-methyl-1-phenylallyl (phenylmethallyl) potassium, K(oInd^{Me}), was isolated as a bright orange, pyrophoric powder in good yield (see Experimental section for further details).

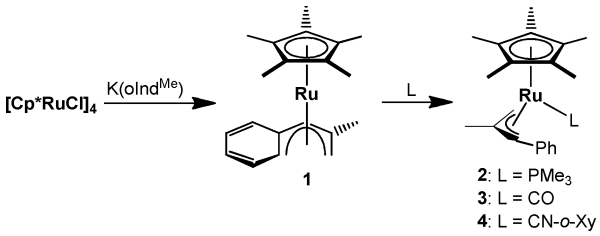


Scheme 1 Synthesis of phenylmethallyl potassium, K(oInd^{Me}). Reagents and conditions: (a) 1. Et_2O, 0 °C → reflux, overnight; 2. HCl; 3. $KHSO_4/MgSO_4$. (b) KO^{t}Bu/*n*BuLi, −78 °C.

K(oInd^{Me}) is indefinitely storable under an inert atmosphere (N_2), and its THF solutions are stable for at least 24 h. The NMR spectroscopic data are in agreement with earlier studies,[9] which suggested that the anion is held in the required U-conformation (corresponding to an *anti*-orientation of the phenyl ring with respect to the methyl substituent) in a similar fashion to that described for the 2,4-dimethylpentadienyl anion.[7] Accordingly, the methyl group can be expected to be essential for the formation of η^5-oInd^{Me} complexes, since the related unsubstituted phenylallyl anion adopts an S-conformation (corresponding to a *syn*-orientation),[11] and coordinates as an η^3-allyl ligand in several examples.[12]

Preparation of an open indenyl ruthenium(II) complex

Since many cyclopentadienyl-ruthenium sandwich complexes incorporating a broad variety of pentadienyl and heteropentadienyl ligands are known,[13] the preparation of the corresponding half-open ruthenocene [(η^5-C_5Me_5)Ru(η^5-oInd^{Me})] (**1**) was attempted by the transmetallation reaction of tetrameric [(η^5-C_5Me_5)RuCl]$_4$ with four equivalents of K(oInd^{Me}) (Scheme 2). Complex **1** could be isolated after sublimation as an orange-red solid in 55% yield. NMR spectroscopy clearly established the coordination of oInd^{Me} as an η^5-pentadienyl ligand, since, for instance, the ^{1}H NMR spectrum exhibits two distinct peaks for the *ortho*-hydrogen atoms of the phenyl ring, whereby an extreme upfield shift from 6.42 to 2.89 ppm is observed for the phenyl CH group forming part of



Scheme 2 Synthesis of [(η^5-C_5Me_5)Ru(η^5-oInd^{Me})] (**1**) and the haptictiy switch of the open indenyl ligand upon addition of a ligand L.

the metal-bound pentadienyl system. In addition, six instead of formerly four resonances can be assigned to the phenyl carbon atoms in the ^{13}C NMR spectrum.

An X-ray diffraction study of **1** confirmed the presence of a half-open ruthenocene, in which the oInd^{Me} ligand displays a η^5-coordination mode (Fig. 2), albeit in a markedly distorted fashion with the Ru–C distances ranging from 2.178(3) Å (Ru–C3) to 2.312(3) Å (Ru–C5). Despite this slight slippage of the Ru atom towards the allylic moiety (C1–C3), significant interaction with the C4 and C5 carbon atoms is indicated by a considerable bending of the phenyl group towards the metal atom; the resulting fold angle, which has also been used to describe structural distortions in indenyl complexes,[14] between the planes containing C1–C3 and C4–C9 is 14.8°. In addition, phenyl coordination leads to a noticeable perturbation of the electron delocalization within the six-membered ring as revealed by a pronounced bond alternation, *e.g.* with C–C bond lengths of 1.365(5), 1.416(5) and 1.351(5) Å within the C6–C7–C8–C9 moiety. The crystal structure of the related indenyl complex [(η^5-C_5Me_5)Ru(η^5-C_9H_7)] displays a similar, but slightly higher degree of bond alternation.[15]

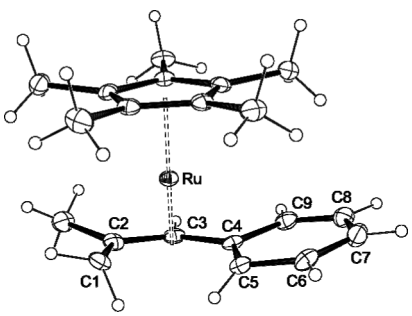


Fig. 2 ORTEP diagram of **1** with thermal displacement parameters drawn at 30% probability. Selected bond lengths (Å) and angles (°): Ru–C(C_5Me_5) 2.161(3)–2.210(3), Ru–C1 2.199(3), Ru–C2 2.179(3), Ru–C3 2.178(3), Ru–C4 2.216(3), Ru–C5 2.312(3), C1–C2 1.425(5), C2–C3 1.420(5), C3–C4 1.442(5), C4–C5 1.445(5), C5–C6 1.430(5), C6–C7 1.365(5), C7–C8 1.416(5), C8–C9 1.351(5), C4–C9 1.447(5); C1–C2–C3 121.9(3), C2–C3–C4 127.2(3), C3–C4–C5 122.8(3).

Overall, the structural features resemble those found in related half-open ruthenocenes containing the (η^5-C_5Me_5)Ru fragment.[13b,c,g,i] Similarly, the two ligands in **1** are reasonably coplanar, with a tilt angle of 5.6° between the planes containing the metal-bound carbon atoms. Although the metal–carbon distances for the two ligands are comparable, the Ru atom is located much closer to the plane of the acyclic ligand (1.616 *versus* 1.821 Å) as expected for a wider, open π-system.[2] In **1**, this opening is more pronounced than observed in the related 2,4-dimethylpentadienyl

complex [(η⁵-C_5Me_5)Ru(η⁵-2,4-C_7H_{11})] as indicated by a larger separation between the two terminal carbon atoms C1 and C5 (2.868 *versus* 2.783 Å).[13i] It should also be noted that the open indenyl coordination motif in **1** is related to that in a number of cymantrene-based molecules containing η⁵-hydronapthalenyl ligands.[16] In these cases, however, the presence of a bridging CH_2 unit at the electronically open edge affords smaller C–C separations, *e.g.* 2.393 Å for [Mn(η⁵-$C_{10}H_9$)$(CO)_3$].[16c] In contrast to **1**, these complexes are not prepared by direct incorporation of the hydronapthalenyl ligand, but generally from nucleophilic attack of [Mn(η⁶-$C_{10}H_8$)(CO_3)]⁺ (η⁶-$C_{10}H_8$ = naphthalene), which is also a well-established method for the preparation of related open cymantrenes of the type [Mn(η⁵-cyclo-dienyl)(CO_3)].[2c]

η⁵ to η³ hapticity interconversion

The sandwich complex **1** obeys the 18-electron rule, and consequently, coordination of additional ligands to the ruthenium atom is not possible unless the open indenyl ligand switches its hapticity from an η⁵ to an η³ coordination mode. The 16-electron intermediate would then provide a vacant coordination site for an incoming substrate. Such an interconversion was observed for the related oxapentadienyl complex [(η⁵-C_5Me_5)Ru(η⁵-2,4-C_6OH_9)] (2,4-C_6OH_9 = 2,4-dimethyloxapentadienyl), in which the C–O π-bond coordination is broken upon reaction with either PMe_3 or CO under reflux for at least 6 h, affording the complexes [(η⁵-C_5Me_5)Ru(η³-2,4-C_6OH_9)(L)] (L = PMe_3, CO).[13h] It is noteworthy that the PMe_3 product was reported to have limited stability, whereas the reaction with CO did not lead to complete conversion. In our hands, addition of one equivalent of PMe_3 to [(η⁵-C_5Me_5)Ru(η⁵-oInd^{Me})] (**1**) at room temperature resulted in a color change from orange to yellow within a few minutes (Scheme 2). $^{31}P\{^1H\}$ NMR spectroscopy clearly confirmed PMe_3 coordination and formation of complex **2** by a downfield shift from −60.1 ppm for the free phosphine to 6.3 ppm. In addition, the ^1H and ^{13}C NMR spectra display a number of couplings with the ^{31}P nucleus. Consequently, the ^1H NMR spectrum exhibits a single broad resonance (6.9–7.0 ppm) in the aromatic region for the five H atoms of the displaced, uncoordinated phenyl group. Similar observations were made upon reaction of **1** with carbon monoxide or 2,6-dimethylphenyl isocyanide (CN-*o*-Xy), and the spectroscopic data together with the elemental analyses are in full agreement with the clean formation of [(η⁵-C_5Me_5)Ru(η³-oInd)(L)] (**2**, L = PMe_3; **3**, L = CO; **4**, L = CN-*o*-Xy) (Scheme 2, see Experimental section for details).

X-ray diffraction analyses of crystals of **2** and **3** confirmed that the open indenyl ligand has undergone an η⁵–η³ hapticity interconversion (Fig. 3 and 4), and the phenyl ring, which has preserved its *anti*-orientation, now clearly tilts out of the allylic plane with an increase of the absolute C1–C2–C3–C4 torsion angle from 4.5° in **1** to 60.6° and 49.9° in **2** and **3**, respectively. The additional ligand is located next to the open edge of the allyl moiety corresponding to the expected *exo*-conformation based on detailed studies on d⁶-[(η⁵-C_5H_5)M(η³-allyl)(L)] complexes (L = CO, PR_3), which revealed that the *exo*-isomer is usually more stable than the *endo*-isomer.[17,18] The Ru–L bond distances, at 2.2955(6) and 1.855(2) Å for the PMe_3 and the CO adduct, respectively, are in line with those reported for the complexes [(η⁵-C_5Me_5)Ru(η³-2,4-C_6OH_9)(PPh_3)] (Ru–P = 2.3205(8) Å),[13h] [(η⁵-C_5H_5)Ru(η³-1,1-Ph_2-C_3H_3)(PPh_3)] (Ru–P = 2.329(2) Å),[19] and [(η⁵-C_5H_5)Ru(η³-2-Me-C_3H_4)(CO)] (Ru–C = 1.841(4) Å).[18c]

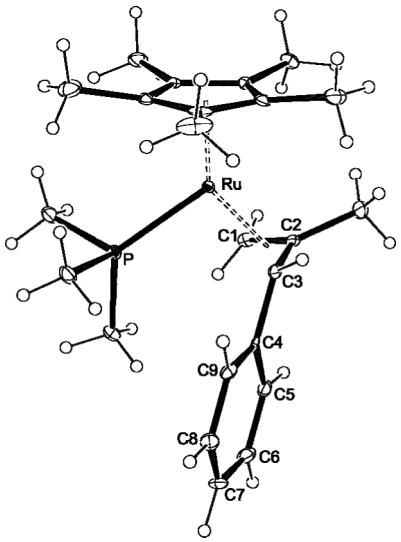


Fig. 3 ORTEP diagram of *anti*-**2** with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (°): Ru–C(C_5Me_5) 2.218(3)–2.256(3), Ru–C1 2.186(2), Ru–C2 2.122(2), Ru–C3 2.208(2), Ru–P 2.2955(6); C1–C2–C3 118.9(2).

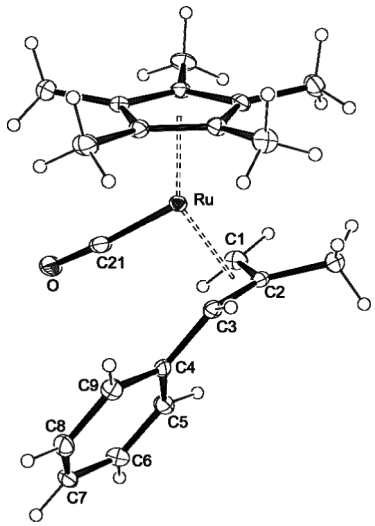


Fig. 4 ORTEP diagram of *anti*-**3** with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (°): Ru–C(C_5Me_5) 2.2071(18)–2.2772(18), Ru–C1 2.218(2), Ru–C2 2.1653(18), Ru–C3 2.2204(17), Ru–C21 1.855(2), C21–O 1.159(3); Ru–C21–O 175.54(18), C1–C2–C3 120.39(17).

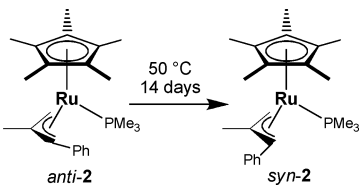
It is remarkable how readily the open indenyl complex **1** is able to provide the 16-electron (η⁵-C_5Me_5)Ru-allyl complex fragment, since the related pentadienyl complex [(η⁵-C_5Me_5)Ru(η⁵-2,4-C_7H_{11})] does not react with PMe_3 or CO, even under reflux conditions.[13h] Additionally, although photoelectron spectroscopy and theoretical studies suggested that the metal-pentadienyl is generally stronger than the metal-heteropentadienyl bond,[20] thus providing a greater reactivity for the latter, we have apparently managed to reverse the usual order.[3] Undoubtedly, the enhanced reactivity of **1** can be ascribed to rearomatization as the main driving force upon ligand addition and concomitant η⁵–η³ hapticity

interconversion. Therefore, the use of open indenyl ligands such as oInd^{Me} offers an alternative and facile access to coordinatively unsaturated cyclopentadienyl-allyl ruthenium(II) species, which are otherwise generated by stepwise methods, *e.g.* by reduction of Ru(IV) precursors such as [(η^5-C_5Me_5)Ru(η^3-allyl)X_2] (X = Cl, Br).[21]

Study of *anti* to *syn* isomerization

In the solid state, the η^3-oInd^{Me} ligand in the PMe_3 and CO complex **2** and **3** displayed the original *anti*-orientation of the methyl and phenyl substituents, and NMR spectroscopic characterization indicated the (almost) exclusive formation of these isomers as the kinetic products.[22] When we checked sealed NMR samples after about half a year at room temperature, no changes were observed for the CO complex **3**, whereas the ^{1}H, ^{13}C and ^{31}P NMR spectra of the phosphine congener **2** revealed the presence of considerable amounts of an additional species.

Heating this sample for several days eventually resulted in the disappearance of the peaks assigned to the original product and in the predominant formation of a new compound (Scheme 3). We were able to grow crystals suitable for X-ray diffraction analysis from this sample, and the resulting molecular structure is shown in Fig. 5. In contrast to *anti*-**2** (*vide supra*, Fig. 3), the phenyl group now points away from the PMe_3 ligand and adopts a *syn*-orientation with respect to the methyl group, while preserving the *exo*-conformation. In analogy to various experimental and theoretical studies on *syn*-*anti* isomerization in palladium, nickel or ruthenium complexes,[23] formation of the isomer *syn*-[(η^5-C_5Me_5)Ru(η^3-oInd^{Me})(PMe_3)] (*syn*-**2**) can be rationalized by a η^1-oInd^{Me} intermediate with an Ru–C3 bond that allows rotation around the C2–C3 bond. Apart from the different position of the phenyl group, the structural parameters of *syn*-**2** and *anti*-**2** are very similar.



Scheme 3 Slow isomerization of *anti*-**2** to *syn*-**2**.

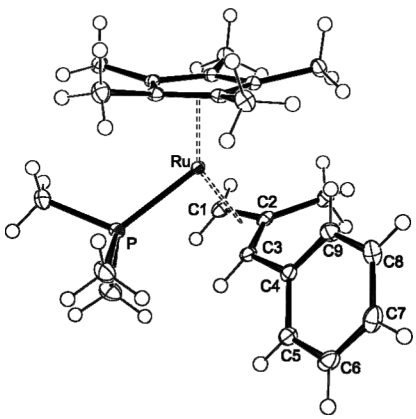


Fig. 5 ORTEP diagram of *syn*-**2** with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (°): Ru–C(C_5Me_5) 2.2055(13)–2.2837(14), Ru–C1 2.1672(14), Ru–C2 2.1308(13), Ru–C3 2.2439(13), Ru–P 2.2953(4); C1–C2–C3 114.73(13).

Since the *anti* to *syn* isomerization proceeds slowly at room temperature, this process can conveniently be followed by NMR spectroscopy. Thus, a sample of *anti*-**2** in C_6D_6 was sealed in an NMR tube, heated at 50° C (323 K) for 21 days and regularly monitored by ^{31}P and ^{1}H NMR spectroscopy (see Electronic supplementary information for details‡). As expected, a new signal at 11.4 ppm in the ^{31}P NMR assigned to *syn*-**2** became predominant, while the resonance of *anti*-**2** at 6.3 ppm decreased over time (Fig. 6). After 14 days, about 98% of the original isomer was converted, as determined by integration of the respective resonances. Since no further increase of the *syn*/*anti* ratio of 98 : 2 was observed for another seven days, we assume that this distribution represents the equilibrated system.

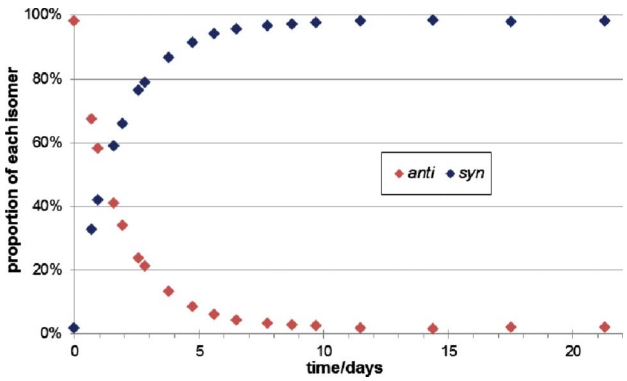


Fig. 6 Change of the proportion of *anti*-**2** and *syn*-**2** in C_6D_6 at 50 °C monitored by ^{31}P NMR spectroscopy over a period of 21 days.

Following the established treatment for a first-order reaction proceeding to equilibrium,[24] a plot $\ln(A_{syn\text{-}2,\infty} - A_{syn\text{-}2,t})$ against time confirmed the isomerization to be a first-order process with a rate constant of $k_{323\,K} = 6.57 \times 10^{-6}$ ($\pm 0.02 \times 10^{-6}$) s^{-1},[25] corresponding to a half-life of 29.3 h and a free activation energy of $\Delta G^\circ = 26.8$ kcal mol^{-1} at $T = 323$ K (Fig. 7).

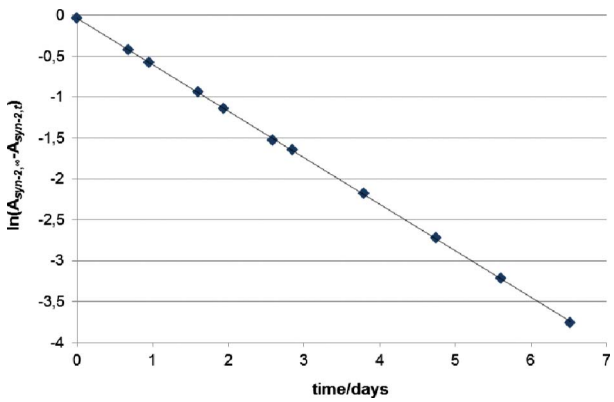


Fig. 7 First-order kinetic plot for the conversion of *anti*-**2** to *syn*-**2** in C_6D_6 at 50 °C monitored by ^{31}P NMR spectroscopy.

To assess the different stabilities of the *anti*- and *syn*-isomers, DFT calculations employing the M06 functional were carried out for **2** and **3** (Table 1). Although the thermodynamic preference for the *syn*-isomer, with $\Delta G_{298} = -1.54$ (**2**) and -1.74 kcal mol^{-1} (**3**), is

Table 1 M06 energies and enthalpies (in kcal mol^{-1}) for the *anti* to *syn* isomerization of complexes **2** and **3**[a]

Complex	ΔE_{el}	ΔE_0	ΔH_{298}	ΔG_{298}
2 (L = PMe_3)	−1.30	−1.36	−1.40	−1.54
3 (L = CO)	−1.45	−1.51	−1.39	−1.74

[a] ΔE_{el}: zero-point uncorrected electronic energies, ΔE_0: relative energies at 0 K, ΔH_{298}: enthalpies at 298 K, ΔG_{298}: Gibbs free energies at 298 K.

fairly low in both cases, these calculations confirm that the *anti*-isomers are only the kinetic products, which can be expected to isomerize slowly to the *syn*-product, as observed for the phosphine species **2**. The Gibbs–Helmholtz equation ($\Delta G_{298} = -RT\ln K$) affords an equilibrium constant of $K_{298\,K} = c_{syn}/c_{anti} = 13.4$, which corresponds to 93% conversion and is in good agreement with the experimentally derived value of $K_{323\,K} = 49$ (based on 98% conversion, *vide supra*).

The disparate behaviour of the CO congener **3**, which does not rearrange to a *syn*-isomer at room temperature, could be ascribed to a higher activation barrier, since a stronger π-acceptor can be expected to disfavour the η^3-η^1-η^3 process,[23i,26] whereas a strong σ-donor such as PMe_3 should stabilize the η^1-oInd^{Me} intermediate (or transition state). In addition, the different steric properties of the PMe_3 and CO ligands (see Fig. 3 and 4) might have a considerable impact on the rates of the *anti* to *syn* isomerization.

Conclusions

The phenylmethallyl ligand oInd^{Me} was shown to be capable of binding to transition metals in a η^5-fashion, as exemplified by preparation of the half-open ruthenocene [(η^5-C_5Me_5)Ru(η^5-oInd^{Me}] (**1**). In analogy to indenyl complexes,[4] this "open indenyl" system is susceptible to ligand addition by undergoing a ready η^5 to η^3 hapticity interconversion, a reaction that has rarely been observed for the corresponding pentadienyl ("open cyclopentadienyl") complexes. Thus, open indenyl complexes such as **1** can be expected to exhibit interesting reactivity by providing a coordinatively unsaturated cyclopentadienyl-allyl complex fragment under mild conditions, and, for instance, C–C coupling reactions with alkynes to form new pentadienyl or vinylidene species could be envisaged.[27,28] Furthermore, in view of the relevance of η^5–η^3 haptotropic rearrangements[29] and of allyl ruthenium species as intermediates in homogeneous catalysis,[8] the use of open indenyl complexes in organotransition metal catalysed reactions can be anticipated.

Experimental section

All synthetic and spectroscopic manipulations were carried out under an atmosphere of prepurified nitrogen, either in a Schlenk apparatus or in a glovebox. Solvents were dried and deoxygenated either by distillation under a nitrogen atmosphere from sodium benzophenone ketyl (THF) or by an MBraun GmbH solvent purification system (all other solvents). NMR spectra were recorded on Bruker DPX 200, Bruker AV 300 and Bruker DRX 400 spectrometers. The chemical shifts are expressed in parts per million (ppm) and are referenced to residual ^{1}H of the solvent, the ^{13}C resonance of the solvent, or external H_3PO_4. If required, the assignment of signals was supported by 2D experiments (COSY, HSQC, HMBC, NOESY). A Bruker Vertex 70 spectrometer was used for recording the IR spectra. Elemental analyses were performed by combustion and gas chromatographical analysis with an Elementar varioMICRO instrument. The mixture of the isomers 2-methyl-1-phenyl-1-propene and 2-methyl-3-phenyl-1-propene was prepared according to the literature,[9b] as was [(η^5-C_5Me_5)RuCl]$_4$.[30] All other reagents were obtained commercially and used as received.

X-ray diffraction studies

Data were recorded at 100 K on Oxford Diffraction diffractometers using monochromated Mo-Kα or mirror-focussed Cu-Kα radiation. The structures were refined anisotropically using the SHELXL-97 program.[31] Hydrogen atoms were either (i) located and refined isotropically (H1A, H1B, H3, and for **1** H5; in some cases with constraints to C–H bond lengths); (ii) included as idealized methyl groups allowed to rotate but not tip or (iii) placed geometrically and allowed to ride on their attached carbon atoms. For compound **3**, the Flack parameter refined to 0.000(8). Crystal and structure refinement data are summarized in Table 2.

Theoretical calculations

All computations were performed using the density functional method M06 as implemented in the Gaussian09 program.[32] For all main-group elements (C, H, P and O), the all-electron triple-ζ basis set (6-311G**) was used,[33] whereas for ruthenium a small-core relativistic ECP together with the corresponding double-ζ valence basis set was employed (Stuttgart RSC 1997 ECP).[34]

2-Methyl-1-phenylallylpotassium, K(oInd^{Me})

A suspension of potassium *tert*-butoxide (6.03 g, 53.7 mmol) in 60 mL of pentane was prepared, and 2-methyl-1-phenyl-1-propene/2-methyl-3-phenyl-1-propene (7.10 g, 53.7 mmol) was added *via* a syringe. The mixture was cooled to −78 °C and n-butyllithium (22.6 mL, 2.5 M, 56.5 mmol) in hexane was added slowly and carefully. After stirring overnight, during which time the mixture was allowed to warm up, the orange precipitate was collected on a frit and washed with 2 × 20 mL, 2 × 15 mL and 3 × 10 mL of pentane. Finally, the bright orange, pyrophoric product was dried under vacuum (7.4 g, 81%). ^{1}H NMR (400 MHz, d_8-THF, ambient): δ = 6.63 (br s, 2 H, *m*-Phenyl), 6.42 (br s, 2 H, *o*-Phenyl), 5.76 (t, $^3J_{HH}$ = 7.0 Hz, 1 H, *para*-phenyl), 3.81 (d, $^4J_{HH}$ = 1.7 Hz, 1 H, H3), 3.38 (d, $^2J_{HH}$ = 2.5 Hz, 1 H, *anti*-H1), 3.21 (br s, 1 H, *syn*-H1), 1.77 (s, 3 H, H10). ^{13}C NMR (100 MHz, d_8-THF, ambient): δ = 146.9 (C4), 143.1 (C2), 128.9 (br, *m*-Phenyl), 108.7 (*p*-Phenyl), 80.8 (C3), 73.6 (C1), 29.5 (C10). The hindered rotation around the C3–C4 bond at room temperature results in a broad resonance for the *meta*-carbon atom, whereas the *ortho*-carbon atom is not observed. At 222 K four separate peaks (130, 128, 123 and 113 ppm) are detected. Because of the extreme air-sensitivity, it was not possible to obtain an accurate elemental analysis.

[(η^5-C_5Me_5)Ru(η^5-oInd^{Me})] (1)

At −78 °C, a dark yellow solution of K(oInd^{Me}) (0.188 g, 1.10 mmol) in 10 mL of THF was added dropwise with a syringe to

Table 2 Crystal and structure refinement for compounds **1**, **2** and **3**

	1	*anti*-**2**	*anti*-**3**	*syn*-**2**
Empirical formula	$C_{20}H_{26}Ru$	$C_{23}H_{35}PRu$	$C_{21}H_{26}ORu$	$C_{23}H_{35}PRu$
Formula weight	367.48	443.55	395.49	443.55
T/K	100(2)	100(2)	100(2)	100(2)
Wavelength λ/Å	1.54184	0.71073	1.54184	0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pccn$	$Pna2_1$	$P2_1/n$
a/Å	13.4601(2)	34.0568(14)	11.5667(2)	8.3388(2)
b/Å	7.1135(1)	14.0658(6)	12.0145(2)	17.1916(6)
c/Å	17.8388(2)	8.9452(4)	13.0890(2)	15.4241(6)
α (°)	90	90	90	90
β (°)	104.424(2)	90	90	105.443(4)
γ (°)	90	90	90	90
Volume/Å^3	1654.20(4)	4285.1(3)	1818.95(5)	2131.33(12)
Z	4	8	4	4
Reflections collected	20622	108761	20543	63644
Independent reflections	3419 [R_{int} = 0.0347]	4371 [R_{int} = 0.1076]	4166 [R_{int} = 0.0436]	4865 [R_{int} = 0.0349]
ρ_c/g cm^{-3}	1.476	1.375	1.444	1.382
μ/mm^{-1}	7.572	0.810	6.973	0.814
$R(F_o)$, [$I > 2\sigma(I)$]	0.0341	0.0246	0.0193	0.0188
R_w (F_o^2)	0.0903	0.0265	0.0534	0.0441
Goodness of fit on F^2	1.077	0.849	1.053	1.046
$\Delta\rho$/e Å^{-3}	2.823/−0.808	0.472/−0.425	0.319/−0.627	0.360/−0.345

a dark red suspension of [(η^5-C_5Me_5)RuCl]$_4$ (0.300 g, 0.28 mmol) in 30 mL of THF. After the slow warm-up and stirring for a total time of 3.5 h, the solvent was removed from the dark red solution. Drying at 50 °C for 1.5 h and subsequent sublimation (0.1 mbar, 100 °C) yielded a red-orange solid (0.222 g, 54%). Single crystals were obtained by slow sublimation in a sealed glass tube. ^{1}H NMR (400 MHz, C_6D_6, ambient): δ = 6.93 (br d, 1 H, Phenyl), 6.84 (br t, 1 H, Phenyl), 6.78 (br t, 1 H, Phenyl), 6.68 (t of t, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 0.9 Hz, 1 H, Phenyl), 5.22 (s, 1 H, H3), 2.89 (d, $^3J_{HH}$ = 5.1 Hz, 1 H, H5), 2.49 (d of d, $^2J_{HH}$ = 3.2 Hz, $^4J_{HH}$ = 0.9 Hz, 1 H, *syn*-H1), 1.81 (s, 3 H, H10), 1.43 (s, 15 H, C_5Me_5), 0.48 (d, $^2J_{HH}$ = 3.1 Hz, 1 H, *anti*-H1). ^{13}C NMR (100 MHz, C_6D_6, ambient): δ = 137.5 (Phenyl), 127.9 (Phenyl), 125.2 (Phenyl), 118.7 (Phenyl), 100.9 (C2 or C4), 94.9 (C2 or C4), 85.3 (C_5Me_5), 85.0 (C3), 66.8 (C5), 44.3 (C1), 25.8 (C10), 10.0 (C_5Me_5). Elemental analysis (%): calculated for $C_{20}H_{26}Ru$ (366.68): C = 65.37, H = 7.13; found: C = 65.24, H = 7.06.

[(η^5-C_5Me_5)Ru(η^3-oInd^{Me})(PMe_3)] (2)

Compound **1** (0.100 g, 0.27 mmol) was dissolved in 10 mL of pentane. The addition of PMe_3 (29 µL, 0.28 mmol) with a micro-syringe resulted in a color change from dark orange to yellow within 10 min. The solvent was removed *in vacuo* and a yellow solid was isolated (0.077 g, 64%). Single crystals were obtained by cooling a saturated pentane solution to −15 °C. ^{1}H NMR (400 MHz, C_6D_6, ambient): δ = 7.13–6.85 (br m, 5 H, Phenyl), 4.17 (s, 1 H, H3), 2.37 (m, 1 H, *syn*-H1), 2.03 (s, 3 H, H10), 1.68 (d, $^4J_{PH}$ = 1.2 Hz, 15 H, C_5Me_5), 1.43–1.38 (br d, $^3J_{PH}$ = 20.5 Hz, 1 H, *anti*-H1), 0.68 (d, $^2J_{PH}$ = 7.6 Hz, 9 H, PMe_3). ^{13}C NMR (100 MHz, C_6D_6, ambient): δ = 152.1 (d, $^3J_{PC}$ = 9.6 Hz, *ipso*-Phenyl), 128.3 (Phenyl), 128.0 (Phenyl), 122.5 (Phenyl), 89.7 (d, $^2J_{PC}$ = 2.0 Hz, C_5Me_5), 76.1 (d, $^2J_{PC}$ = 2.0 Hz, C2), 50.2 (d, $^2J_{PC}$ = 6.0 Hz, C3), 33.6 (d, $^2J_{PC}$ = 6.6 Hz, C1), 26.0 (d, $^3J_{PC}$ = 2.0 Hz, C10), 18.9 (d, $^1J_{PC}$ = 25.0 Hz, PMe_3), 11.3 (C_5Me_5). ^{31}P{^{1}H} NMR (161 MHz, C_6D_6, ambient): δ = 6.2 (s, PMe_3). Elemental analysis (%): calculated for $C_{23}H_{35}PRu$ (443.57): C = 62.28, H = 7.95; found: C = 62.29, H = 7.97.

Isomerization from *anti*-2 to *syn*-2

Isomerization was achieved by heating a sample of *anti*-**2** to 50 °C in either hexane or C_6D_6 over a period of 14 days. Single crystals of *syn*-**2** were obtained by cooling a saturated pentane solution to −30 °C. ^{1}H NMR (400 MHz, C_6D_6, ambient): δ = 7.44 (d of m, 2 H, $^3J_{HH}$ = 7.8 Hz, *o*-Phenyl), 7.25 (m, 2 H, *m*-Phenyl), 7.08 (t of t of br d $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.3 Hz, 1 H, *p*-Phenyl), 2.25 (s, 3 H, H10), 2.06 (d, $^3J_{PH}$ = 18.0 Hz, 1 H, H3), 1.79 (br d, $^3J_{PH}$ = 1.8 Hz, 1 H, *syn*-H1, 1.58 (d, $^4J_{PH}$ = 1.3 Hz, 15 H, C_5Me_5), 0.97 (d, $^2J_{PH}$ = 7.2 Hz, 9 H, PMe_3), 0.69 (d of m, $^3J_{PH}$ = 19.8 Hz, 1 H, *anti*-H1). ^{13}C NMR (100 MHz, C_6D_6, ambient): 146.8 (s, *ipso*-Phenyl), 130.0 (*o*-Phenyl), 127.7 (*m*-Phenyl), 123.4 (*p*-Phenyl), 89.0 (d, $^2J_{PC}$ = 2.3 Hz, C_5Me_5), 79.3 (d, $^2J_{PC}$ = 2.7 Hz, C2), 49.9 (d, $^2J_{PC}$ = 5.4 Hz, C3), 33.1 (d, $^2J_{PC}$ = 7.1 Hz, C1), 22.2 (d, $^3J_{PC}$ = 1.6 Hz, C10), 18.8 (d, $^1J_{PC}$ = 26.1 Hz, PMe_3), 11.0 (C_5Me_5). ^{31}P{^{1}H} NMR (161 MHz, C_6D_6, ambient): δ = 11.3 (s, PMe_3).

[(η^5-C_5Me_5)Ru(η^3-oInd^{Me})(CO)] (3)

Compound **1** (0.100 g, 0.27 mmol) was dissolved in 10 mL of pentane. Then CO (0.6 bar) was bubbled through the solution for one minute accompanied by a color change from dark orange to yellow. Stirring was continued for another minute and the solvent was subsequently removed under vacuum yielding a yellow solid (77 mg, 71%). Single crystals were obtained by cooling a saturated pentane solution to −15 °C. ^{1}H NMR (400 MHz, C_6D_6, ambient): δ = 7.13–7.08 (br m, 4 H, Phenyl), 6.93–6.89 (br m, 1 H, Phenyl), 4.37 (s, 1 H, H3), 2.62 (m, 1 H, *syn*-H1), 2.60 (m, 1 H, *anti*-H1), 1.68 (s, 3 H, H10), 1.64 (s, 15H, C_5Me_5). ^{13}C NMR (100 MHz, C_6D_6, ambient): δ = 209.2 (CO), 148.9 (*ipso*-Phenyl), 128.5 (Phenyl), 125.7 (Phenyl), 123.7 (Phenyl), 94.6 (C_5Me_5), 85.4 (C2), 58.2 (C3), 37.2 (C1), 26.1 (C10), 10.7 (C_5Me_5). Elemental analysis

(%): calculated for $C_{21}H_{26}ORu$ (395.50): C = 63.77, H = 6.63; found: C = 63.96, H = 6.49. IR (Nujol): ν(CO/cm^{-1}) = 1946.

[(η^5-C_5Me_5)Ru(η^3-oInd^{Me})(CN-*o*-Xy)] (4)

Compound **1** (0.100 g, 0.27 mmol) was dissolved in 10 mL of pentane. The addition of CN-*o*-Xy (0.035 g, 0.27 mmol) in 3 mL of pentane with a pipette resulted in a color change from dark orange to dark yellow within 5 min. The solvent was removed *in vacuo* and the yellow solid was crystallized from pentane at −30 °C (0.101 g, 74%). ^{1}H NMR (400 MHz, C_6D_6, ambient): δ = 7.03 (d of m, $^3J_{HH}$ = 7.9 Hz, 2 H, Phenyl), 6.78 (t of br m, $^3J_{HH}$ = 7.7 Hz, 2 H, Phenyl), 6.70 (m, 3 H, Phenyl), 6.48 (t of m, $^3J_{HH}$ = 7.4 Hz, 1 H, Phenyl), 4.40 (s, 1 H, H3), 2.73 (m, 1 H, *syn*-H1), 2.55 (m, 1 H, *anti*-H1), 2.06 (s, 6 H, CH_3), 1.92 (s, 3 H, H10), 1.81 (s, 15 H, C_5Me_5). ^{13}C NMR (100 MHz, C_6D_6, ambient): δ = 150.3 (*ipso*-Phenyl), 133.5 (*ipso*-Phenyl), 128.6 (Phenyl), 127.7 (Phenyl), 125.5 (Phenyl), 125.3 (Phenyl), 122.3 (Phenyl), 92.6 (C_5Me_5), 82.3 (C2), 57.0 (C3), 36.9 (C1), 27.0 (C10), 18.9 (CH_3), 11.1 (C_5Me_5). One carbon signal is probably hidden under the solvent peak; the resonance for the isocyanide carbon atom was not observed. Elemental analysis (%): calculated for $C_{29}H_{35}NRu$ (498.67): C = 69.85, H = 7.07, N = 2.81; found: C = 69.97, H = 7.11, N = 2.88. IR (ATR): ν(CN/cm^{-1}) = 2003.

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