Activation and transfer of O_2 to organic electrophiles by $[RuH(dcpe)_2]^+$†

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The crystal structure of the 16-electron hydride $[RuH(dcpe)_2]PF_6$ ($\mathbf{1}\cdot PF_6$) [dcpe = 1,2-bis(dicyclohexylphosphino)ethane] shows a short contact between Ru and a cyclohexyl CH_2, which was not observed in the disordered tetraphenylborate salt $[RuH(dcpe)_2]BPh_4$ ($\mathbf{1}\cdot BPh_4$). The comparison of the X-ray structure of $\mathbf{1}\cdot PF_6$ with those of $[RuCl(dcpe)_2]PF_6$ (**2**) and *trans*-$[RuCl_2(dcpe)_2]$ (**3**) indicates that electronic effects co-operate with the steric ones in the stabilization of these 16-electron species. The hydrido dioxygen complex $[RuH(\eta^2\text{-}O_2)(dcpe)_2]^+$ (**4**), formed by reaction of **1** with O_2, does not react with nucleophiles such as olefins and PPh_3, but does show nucleophilic properties, reacting with activated olefins (TCNE, 2-methyl-1,4-naphthoquinone) and with carbonyl compounds [heptanal, PhC(O)Cl]. The reaction of **4** with heptanal shows an unprecedented reaction mode for a dioxygen complex of a late transition metal, as the O_2-activating complex **1** is partially regenerated upon oxygen transfer from **4** to the substrate. All these reactions show that oxygen transfer from **4** to an organic substrate effectively competes with oxidation of the dcpe ligand.

The activation of dioxygen at a transition metal complex is one of the dream reactions that have been pursued during the last 30 years.[1] In spite of much effort spent, progress in the field has been very slow, and, despite important achievements, the nature of the metal–dioxygen interaction remains generally elusive. This was also the case in the recent discovery that ruthenium-substituted polyoxometallates catalyse the hydroxylation of adamantane with dioxygenase-like activity.[2] The 30-year-old discovery of O_2 activation by phosphino complexes of the late transition metals has led to the preparation of a large number of dioxygen complexes.[1] However, attempts to use these dioxygen complexes in metal-catalysed oxidation reactions of organic substrates have remained largely unsuccessful with long periods of oblivion followed by recurring bursts of interest.

The co-ordinatively unsaturated d^6 complexes $[RuH(P{-}P)_2]^+$ [P—P = 1,2-bis(dicyclohexylphosphino)ethane (dcpe) or 1,2-bis(diisopropylphosphino)ethane (dippe)][3a] and $[OsX(P{-}P)_2]^+$ [P—P = dcpe[3b] or 1,2-bis(diphenylphosphino)ethane (dppe)[3c]] have been recently found to react with molecular oxygen to give dioxygen complexes[4] of the type $[MX(\eta^2\text{-}O_2)(P{-}P)_2]^+$.[3] The 16-electron species $[MX(P{-}P)_2]^+$ (M = Ru, Os) are unique in their ability to form both dioxygen and dihydrogen[5,6] complexes. Dioxygen complexes of d^6 metals[3,7,8] are less common than those of d^8 and d^{10} metal ions, such as Ir^I and Pt^O complexes,[1] but also Ru^O and Os^O.[9] Parallel to the study of the reactivity of the five-co-ordinate fragments $[MX(dcpe)_2]^+$ (M = Ru,[10a] Os;[10b] X = Cl, H) with H_2 [10c] and, more recently, O_2,[3b] theoretical studies of 16-electron species have contributed substantially to the understanding of the steric and electronic factors that affect the stability of these 16-electron complexes.[11] We report herein a new X-ray investigation suggesting that the five-co-ordinate hydride $[RuH(dcpe)_2]PF_6$ ($\mathbf{1}\cdot PF_6$) is possibly stabilized by a weak agostic interaction. This structural feature was obscured by disorder in a recent X-ray study of the tetraphenylborate analogue $\mathbf{1}\cdot BPh_4$.[12]

Although a number of d^6 dioxygen complexes have been recently prepared,[3,8] their reactivity has not yet been investigated. Also, the reaction of the five-co-ordinate species $[MX(dcpe)_2]^+$ (M = Ru and Os) with O_2 is a suitable starting point for understanding the role played by the metal centre in the activation of dioxygen into a number of aerobic oxidation reactions catalysed by phosphine complexes of ruthenium(II).[13] Five-co-ordinate ruthenium(II) species such as $[RuCl_2(PPh_3)_3]$ and $[RuCl(dppp)_2]^+$ [dppp = 1,3-bis(diphenylphosphino)propane] have been used in aerobic catalytic oxidation reactions.[13a,b] Although these co-ordinatively unsaturated complexes have been proposed to react with molecular oxygen, the formation of peroxo adducts of these complexes under catalysis conditions has not been conclusively proven.[1b]

More generally, an investigation of the reactivity of d^6 Ru^{II} and Os^{II} dioxygen complexes is of interest in view of their intermediate position between the "electrophilic" dioxygen complexes of the early transition elements and the "nucleophilic" analogues of the late ones, and is of relevance to the recent mechanistic debate[14] about the catalytic co-oxidation reactions developed primarily by Mukaiyama and co-workers using a variety of substrates and reductants, such as aldehydes, alcohols, and ketones.[15] Thus, we have investigated the reactivity of the dioxygen hydride $[RuH(\eta^2\text{-}O_2)(dcpe)_2]PF_6$ (**4**) towards electrophilic substrates such as heptanal, PhC(O)Cl, tetracyanoethylene (TCNE), and 2-methyl-1,4-naphthoquinone (menadione).

Results and discussion

Structural aspects of $[RuH(dcpe)_2]^+$

Recently, Winter and Hornung have reported the X-ray structure of $[RuH(dcpe)_2]BPh_4$ ($\mathbf{1}\cdot BPh_4$), in which both crystallo-

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† *Supplementary material available:* NMR spectra. For direct electronic access see http://www.rsc.org/suppdata/nj/1999/199/, otherwise available from BLDSC (No. SUP 57473, 2 pp) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/njc).

graphically independent cations are located in a special position and possess a crystallographic two-fold axis of symmetry lying in the RuP_4 plane.[12] Since square-pyramidal cations are not C_2-symmetric about any direction in the RuP_4 plane due to the presence of the apical hydride, this arrangement results in a disordered situation in which the hydride ligand must be located with 50% occupancy on both sides of the RuP_4 plane. With the idea that disorder might conceal some structural feature, we prepared the $[PF_6]^-$ analogue $[RuH(dcpe)_2]PF_6$ (**1** · PF_6) by reaction of *trans*-$[RuHCl(dcpe)_2]$ with $TlPF_6$. Selected interatomic distances and angles are given in Table 1, and an ORTEP view is shown in Fig. 1. In order to assess the role of steric and electronic effects in a series of Ru^{II}–dcpe complexes, we have also determined the X-ray structure of *trans*-$[RuCl_2(dcpe)_2]$ (**3**) (Fig. 2).

$[RuH(dcpe)_2]PF_6$, 1 · PF_6. The unit cell of **1** · PF_6 contains the complex cation (in general positions) and two crystallographically independent $[PF_6]^-$ anions at 50% occupancy in special positions. All non-hydride H atoms have been located and refined. The major distortion from the ideal square-pyramidal geometry is the displacement of two of the four P atoms away from the RuP_4 plane. The P(2)—Ru—P(4) angle is closed down to 171.3°, whereas P(1)—Ru—P(3) has an ideal value of 179.69(4)°. The P and Ru atoms are within ±0.11 Å from the best RuP_4 plane, and the Ru—P(1)—P(2) and Ru—P(3)—P(4) planes form an angle of 8.79(2)°. The dihedral angle between these planes plays a major role: although the conformation of both chelate rings is a nearly ideal twist, the closing of the P(2)—Ru—P(4) angle pushes C(1) and C(3) away, by 0.40 and 0.36 Å, from the best RuP_4 plane toward the hydride. The bite angles are normal for five-membered rings (average value is 82.6°).

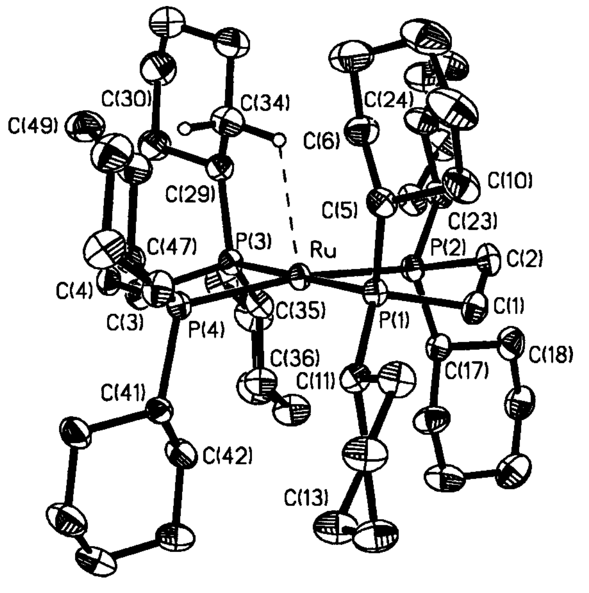


Fig. 1 ORTEP view of the cation **1** in $[RuH(dcpe)_2]PF_6$.

Table 1 Selected interatomic distances (Å) and angles (°) in $[RuH(dcpe)_2]PF_6$, **1** · PF_6

Ru—P(1)	2.3484(10)	C(34)—H(34B)	1.14(6)
Ru—P(2)	2.3710(11)	Ru···C(6)	3.511(5)
Ru—P(3)	2.3454(11)	Ru···C(34)	3.332(5)
Ru—P(4)	2.3746(11)	Ru···H(6B)	2.84(5)
C(6)—H(6B)	0.99(6)	Ru···H(34B)	2.59(5)
P(1)—Ru—P(2)	82.90(4)	Ru—P(2)—C(2)	108.6(2)
P(1)—Ru—P(3)	179.69(4)	Ru—P(2)—C(17)	116.2(1)
P(1)—Ru—P(4)	97.91(4)	Ru—P(2)—C(23)	125.2(2)
P(1)—Ru—H(34B)	110 (1)	Ru—P(3)—C(3)	111.3(2)
P(2)—Ru—P(3)	96.81(4)	Ru—P(3)—C(29)	110.0(1)
P(2)—Ru—P(4)	171.26(4)	Ru—P(3)—C(35)	120.2(2)
P(2)—Ru—H(34B)	89 (1)	Ru—P(4)—C(4)	108.9(1)
P(3)—Ru—P(4)	82.40(4)	Ru—P(4)—C(41)	115.6(1)
P(3)—Ru—H(34B)	69 (1)	Ru—P(4)—C(47)	125.9(1)
P(4)—Ru—H(34B)	99 (1)	P(1)—C(5)—C(6)	110.5(3)
Ru—P(1)—C(1)	110.0(1)	P(1)—C(5)—C(10)	118.6(3)
Ru—P(1)—C(5)	114.1(1)	P(3)—C(29)—C(30)	119.4(3)
Ru—P(1)—C(11)	119.3(1)	P(3)—C(29)—C(34)	108.8(3)

The axial hydride ligand was not located: an electron density peak about 1.0 Å below Ru was found in the final ΔF map, but could not be refined to a chemically reasonable Ru—H distance. However, the hydride ligand is most probably located below the RuP_4 plane (Fig. 1), since the apical position above this plane is involved in two short contacts between Ru and two cyclohexyl groups. The shortest Ru···H contact [2.59(5) Å], which involves the cyclohexyl equatorial β-hydrogen on C(34), suggests a weak γ-agostic interaction (see below).[16] The next shortest Ru···H contact [2.84(5) Å] involves C(6), which can replace C(34) in the interaction to Ru with a minor rearrangement. The shortest Ru···H distances on the opposite side of the RuP_4 plane involve the equatorial H atoms H(22A) and H(42A) and are much longer (3.30 and 3.32 Å, respectively), in agreement with the presence of the hydride ligand.

Comparison to **1** · PF_6 clearly indicates that the tetrahedral distortion observed in **1** · BPh_4 is an artifact of disorder. In fact, the P(1)—Ru—P(3) and P(2)—Ru—P(4) angles of **1** · PF_6 are markedly different [179.69(4)° and 171.26(4)°, respectively], whereas in **1** · BPh_4 the crystallographic two-fold axis bisecting the P(11)—Ru—P(11a) and P(12)—Ru—P(12a) angles forces the angles between the *trans* P atoms to be equivalent. Accordingly, the average of the *trans* P—Ru—P angles in **1** · PF_6 (175.5°) is close to the value of 174.4° observed in **1** · BPh_4. Also, the thermal ellipsoids of P(11) and P(21) in **1** · BPh_4 are elongated perpendicular to the RuP_4 plane, which is not physically reasonable and indicates that the real atomic positions are split between two minima. The same is true for C(11) and C(21). Again, the comparison with **1** · PF_6 is revealing. Since both C(1) and C(3) lie on the same side of the RuP_4 plane in **1** · PF_6, the conformation of the two chelate rings is not compatible with any binary axis lying in the RuP_4 plane: thus, C(11) and C(12) in **1** · BPh_4 are disordered.

The disorder in **1** · BPh_4 masks the most interesting structural feature of **1**, namely the short Ru···H non-bonded distances. In **1** · PF_6, the closest Ru···H contacts are 2.59(5) and 2.84(5) Å on one side of the RuP_4 plane, and 3.30(5) and 3.32(5) Å on the opposite one. Also, the orientation of the cyclohexyl groups is significantly different on either side of the RuP_4 plane. In **1** · BPh_4, the pseudo-symmetry imposes averaged distances (≈3.0 Å) between Ru and H atoms lying on *opposite* sides of the RuP_4 plane, which obscures the Ru···H—C close contact. However, the agostic interaction in **1** · PF_6 is, in the best of cases, very weak. Applying Crabtree's parametrization to the shortest contact gives an effective covalent radius of the C—H bonding electrons r_{bp} of 1.46 Å, an M—H—C angle H of 120°, and a corrected Ru···H(34B) of 2.54 Å. This is suggestive of a weak γ-agostic interaction rather than a simple van der Waals contact.[16b] The presence of an attractive interaction in **1** · PF_6 is further indicated by (*i*) the closing of the Ru—P(3)—C(29) angle, (*ii*) the shortening of the Ru—P(3) distance and (*iii*) the tilting of the C(29)—C(34) cyclohexyl group towards the Ru atom [P(3)—C(29)—C(34) = 108.8(3)°, P(3)—C(29)—C(30) = 119.4(3)°]. The X-ray structures of the 16-electron species $[W(CO)_3(PCy_3)_2]$ and $[Re(CO)_3(PCy_3)_2]^+$ reveal distortions that are qualitatively similar, albeit much larger in magnitude.[17] Being attracted toward the metal, the C(5)—C(10) and C(29)—C(34) cyclohexyl groups push the C(23)—C(28) and

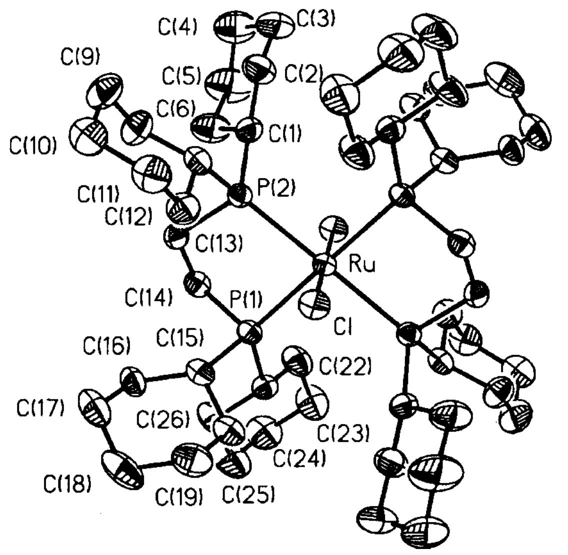


Fig. 2 ORTEP view of [RuCl$_2$(dcpe)$_2$], **3**. Selected bond lengths (Å) and angles (°) are: Ru—P(1) 2.400(2), Ru—P(2) 2.447(2), Ru—Cl 2.435(2), Cl—Ru—P(1) 91.8(1), Cl—Ru—P(2) 96.0(1), P(1)—Ru—Cl′ 88.2(1), P(1)—Ru—P(2) 81.9(1), P(1)—Ru—P(2′) 98.1(1), P(2)—Ru—Cl′ 84.0(1).

C(47)—C(52) ones away, as shown by the P(2)—Ru—P(4) angle, which is closed toward the hydride ligand. As a result, the angles between P(2) and P(4) and the axial hydride must be less than 90°. Thus, the conformation of the cyclohexyl groups probably derives from the weak Ru···H—C interaction rather than from steric factors, as claimed for **1** · BPh$_4$.[12] In fact, the steric crowding due to the cyclohexyl rings cannot be invoked for **1**, since, even in the much more crowded *trans*-[RuCl$_2$(dcpe)$_2$] (**3**), the rotational freedom of the cyclohexyls releases the steric strain (Fig. 2).

[RuCl$_2$(dcpe)$_2$], 3. The unit cell contains discrete [RuCl$_2$(dcpe)$_2$] and two CH$_2$Cl$_2$ molecules with normal nonbonded distances. Since the Ru atom lies on an inversion centre, only one-half of the molecule is crystallographically independent. However, this is compatible with the complex symmetry. The co-ordination geometry is a slightly distorted octahedron, apparently due to the constraint of the P(1)—Ru—P(2) bite angle of 81.9(1)°, a value similar to that found in **1**. The crystal symmetry imposes angles of exactly 180° for all mutually *trans* ligands. The average Ru—P bond length of 2.424(2) Å is up to 0.06 Å longer than in the five-co-ordinate hydride **1** [2.360(1) Å] and falls at the upper end of the range found for a number of ruthenium(II) complexes.[18] Interestingly, the concerted opening of the Cl—Ru—P(2) angle to 96.0(1)° [due to the C(7)—C(12) cyclohexyl ring pointing toward Cl] and the rotation of the cyclohexyl groups release the steric congestion.

Besides confirming the theoretical studies of the MXL$_4$ complexes of d^6 ions that predict a square-pyramidal structure for X = H and a Y-shaped one for X = Cl,[11] the comparison of the structures of **1** · PF$_6$, **2** and **3** is extremely informative about the secondary interactions that stabilize the five-co-ordinate species [RuX(dcpe)$_2$]$^+$, together with the bulkiness of the diphospine ligands. Thus, in **1** · PF$_6$ it is the weak M···H—C interaction that stabilizes the 16-electron complex,[19] whereas in the chloro analogue **2**, it is the Cl → Ru π-donation, as indicated by the short Ru—Cl bond length [2.386(3) Å, (Table 2)].[20] The latter value falls in the lower quartile of the distribution found for 115 Ru^{II} complexes (average Ru—Cl distance of 2.416 Å), and is dramatically shorter than in the dichloro analogue **3** [2.435 (2) Å].

Table 2 Average bond lengths in **1**, **2** and **3** (Å)

	[RuH(dcpe)$_2$]$^+$ (**1**)	[RuCl(dcpe)$_2$]$^+$ (**2**)	[RuCl$_2$(dcpe)$_2$] (**3**)
Ru—P	2.360(1)	2.424(4) (ax) 2.294(3) (eq)	2.424 (2)
Ru—Cl		2.386(3)	2.435 (2)

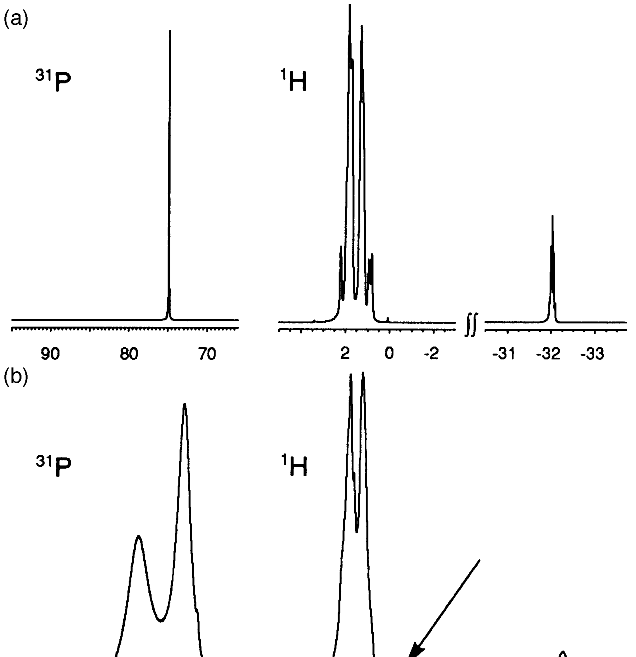


Fig. 3 (Left) ^{31}P{^{1}H} and (right) ^{1}H NMR spectra of **1** (250 MHz, LB = 4 Hz, CD$_2$Cl$_2$) at (*a*) room temperature and (*b*) 183 K.

Solution studies of 1 · PF$_6$. The existence of some degree of Ru···H—C interaction in **1** · PF$_6$ in solution was investigated by IR and NMR spectroscopies. A weak IR band at 2709 cm^{-1} (CH$_2$Cl$_2$ solution) can be tentatively attributed to the stretching vibration of the agostic C—H bond. At room temperature, the ^{31}P{^{1}H} NMR spectrum is a sharp singlet at δ 73.6, which broadens upon cooling, indicating that a dynamic process slows down on the NMR time scale. At −80 °C, two broad signals are observed (Fig. 3), but no resolved ^{31}P{^{1}H} spectrum is achieved down to the lowest available temperature (*ca.* −90 °C). The ^{1}H NMR spectra recorded between 20 and −60 °C show a quintet for the hydride and broad signals without unusual features for the methylene protons. The quintet structure is lost below this temperature, and a broad signal integrating as 1 H decoalesces from the high frequency side of the featureless C*H*$_2$ hump. However, the assignment of the "agostic" C—H is not conclusive. In fact, the signal of the single H is still broad at −90 °C: its chemical shift of δ −0.36 is indicative of the Ru···H—C contact, but the width of this ^{1}H NMR signal ($w_{1/2}$ = 268 Hz at 250 MHz) prevents the measurement of the *J*(C,H) coupling constant. Even at 500 MHz the half-line width $w_{1/2}$ is as large as 150 MHz. This suggests that the chemical exchange between different C—H groups is not frozen out even at −90 °C. At the same temperature, the occurrence of a dynamic process is observed also in the ^{31}P NMR spectrum [Fig. 3(*b*)]. In a further attempt to freeze out the dynamic process, the ^{1}H NMR spectra were recorded in a CD$_2$Cl$_2$–(CD$_3$)$_2$CO mixture (4 : 1) down to the freezing point of the solution (*ca.* −120 °C). Unexpectedly, these spectra show that a further exchange process slows down. Instead of sharpening, the signals of the methylene protons broaden further, and new signals appear in the hydridic region about δ

-30 (see Fig. S1 in the Supplementary Material). In view of this further complication, attempts to record spectra in Freon–CD_2Cl_2 mixtures were not undertaken.

Although the ^1H NMR data possibly suggest that some sort of Ru···H—C interaction is retained in solution, at least at low temperature, this interaction must be very weak. Also, the hydride chemical shift observed for **1** (δ -32.0) is in the range observed for five-co-ordinate complexes, whereas related complexes displaying strong agostic interactions to the vacant site have hydride resonances at considerably lower field (around δ -12).[6a] Although agostic interactions are a common feature of 16-electron species, they have been rarely observed in five-co-ordinate ruthenium(II) complexes either by ^1H NMR spectroscopy or X-ray diffraction. An unusual one is that involving a methylene group of the diphosphine backbone in $[RuH(P—P)_2]^+$ [P—P = 1,4-bis(diphenylphosphino)-butane (dppb) or 2,3-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (diop)].[6a]

Reactivity of $[RuH(\eta^2\text{-}O_2)(dcpe)_2]^+$, 4

Reactivity with nucleophiles. The reactivity of **4** with nucleophiles and electrophiles was investigated.[21] No reaction occurs with electron-rich olefins, such as 1-hexene and styrene, or with PPh_3. The $^{31}P\{^1H\}$ and ^1H NMR spectra of **4** remain unchanged in the presence of these substrates (either in excess or in a 1 : 1 molar ratio) in CD_2Cl_2 solution after several days. The failure of **4** to react with electron-rich olefins and PPh_3 parallels the behaviour of the recently reported $[M(\eta^2\text{-}O_2)(CO)(CH_3CN)(PPh_3)_2]^+$ (M = Rh, Ir),[22] and suggests that the dioxygen ligand in these complexes has *nucleophilic* character (see below).

Reactions with electrophiles. The classification scheme of the relative nucleophilic reactivity of transition metal peroxo complexes, devised by Valentine and co-workers, prompted us to investigate the reactivity of **4** toward carbonyl compounds and electron-poor olefins.[21] The results of this study allow comparison to early reports of the reactions between $[M(\eta^2\text{-}O_2)L_2]$ (M = Ni, Pd, Pt; L = RNC or PPh_3) and PhC(O)Cl, RCHO, or TCNE.[23–26]

When **4** and TCNE (1 equiv.) are dissolved in anhydrous CD_2Cl_2 under argon, a green solution is formed instantaneously, which turns dark brown within 6 h. Work-up yields a dark brown crystalline compound that is not a hydride, as shown by ^1H NMR spectroscopy. The IR spectrum suggests oxidative fragmentation of TCNE: bands at 2209 and 1611 cm^{-1} are typical of a tricyanovinylethanol (tcva) ligand.[27] The presence of an *N*-bound isocyanato ligand is suggested by the peaks in the FAB$^+$ mass spectrum at *m/z* 1005 and 973, corresponding to $[Ru(NCO)(O)(dcpe)_2]^+$ and $[Ru(CN)(dcpe)_2]^+$, and is in agreement with the IR bands at 2209 and 1327 cm^{-1}, attributed to the asymmetric and symmetric N=C=O stretching vibrations.[28,29] The band at 2209 cm^{-1} probably results from the overlap of the CN bands of tcva with $\nu_{as}(N=C=O)$. As recrystallization attempts only yielded intractable oils, no analytically pure product was isolated. The nature of this product is currently under investigation.

The reaction of **4** with 2-methyl-1,4-naphthoquinone (menadione), another electron-poor, highly activated olefin, was monitored by ^1H and $^{31}P\{^1H\}$ NMR in an NMR tube. After 24 h, **1** (20% of starting **4**) and dcpe oxide **5** (30%) are observed, but no trace of menadione oxide is visible in the ^1H NMR spectrum. After 5 days in the dark at room temperature, **4** is consumed and the acetato complex $[Ru(\eta^2\text{-}O_2CMe)(dcpe)_2]^+$ (**6a**) is formed, together with dcpe oxide (Table 3, entry 1). Column chromatography of the reaction solution yielded pure **6a** and unreacted menadione (about 70% of starting amount). The identity of **6a** is supported by comparison of the FAB$^+$ MS and NMR data with those of an authentic sample. The acetato ligand is probably formed by oxidative degradation of menadione. A control reaction showed that **4** reacts slowly with menadione oxide (**4** is consumed after 5 days), giving unidentified products, but only a small amount of **6a** (5%).

Complex **4** reacts with other organic electrophiles such as PhC(O)Cl and aldehydes. The reaction of **4** with PhC(O)Cl gives the carboxylato derivative $[Ru(\eta^2\text{-}O_2CPh)(dcpe)_2]^+$ (**6b**) (by comparison with an authentic sample) (Table 3, entry 2). After 24 h, 80% of starting **4** has reacted and some benzoato complex **6b** is formed, together with **2**, dcpe oxide **5**, and as yet unidentified products. The reaction of **4** with aldehydes, which are weaker electrophiles than acyl chlorides, is most interesting. Acid-free heptanal and **4** (2:1 molar ratio) react quantitatively within 24 h giving a mixture of products: **1**, $[RuCl(\eta^2\text{-}H_2)(dcpe)_2]^+$ (**7**),[10c] and the carboxylato complex $[Ru(\eta^2\text{-}O_2CC_6H_{13})(dcpe)]^+$ (**6c**), together with dcpe oxide **5** (Table 3, entry 3). The occurrence of oxygen transfer to the aldehyde is indicated by the presence in the reaction mixture of **1**, **6c** and $C_6H_{13}C(O)OH$, as detected by GC-MS and ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. Low-intensity broad signals in the ^1H NMR spectrum (δ region 0 to -4) suggest that minor amounts of as yet unidentified paramagnetic products are also formed. When a stoichiometric amount of TEMPO (2,2,6,6,-tetramethyl-1-piperidinyloxyl radical) is added to the reaction solution, the formation of dcpe oxide is inhibited, and the carboxylato species **6c** is the main product after 24 h (Table 3, entry 4). By contrast, when the radical initiator azaisobutyronitrile, AIBN, is added, dcpe oxide is the major product (Table 3, entry 5). Attempts to detect the corresponding peroxy carboxylic acid as an intermediate were not successful.[30]

The reactions with PhC(O)Cl, RCHO, and TCNE indicate that **4** is a nucleophile of strength comparable to that of $[M(\eta^2\text{-}O_2)L_2]$ (M = Ni, Pd, Pt; L = RNC or PPh_3).[23–26] The reaction of **4** with aldehydes is particularly interesting, as it is an example of an "atom-transfer redox reaction" according to

Table 3 Oxygen-transfer reactions of **4**[a]

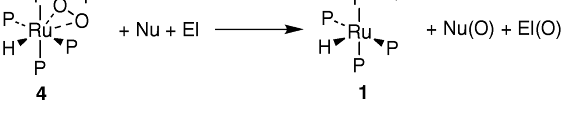
Run	Reagent(s)	Ratio[b]	*t*/days	Conv/%	Products (yield/%)[c]
1	Menadione	1 : 1	5	>99	**6a** (30), **5** (50)
2	PhC(O)Cl	1 : 1	1	80	**6b** (10), **2** (10), **5** (20)
3	$C_6H_{13}CHO$	1 : 2	1	>99	**1** (29), **6c** (7), **7** (17), **5** (40)
4	$C_6H_{13}CHO$ [d]	1 : 2	1	>90	**6c** (50), **5** (10)
5	$C_6H_{13}CHO$ [e]	1 : 2	1	>90	**5** (80)
6	PhC(O)Cl–PPh_3	1 : 1 : 1	5	>90	$Ph_3P=O$ (25),[f] **6b** (25), **2** (23), **1** (15), **5** (12)
7	PhC(O)Cl–styrene	1 : 1 : 1	7	>90	**2** (30), **6b** (28), **1** (3), **5** (10)
8	$C_6H_{13}CHO$–styrene	1 : 1 : 1	6	>99	**5** (25), **1** (20), **6c** (5), **7** (13)

[a] Reactions monitored by ^1H and $^{31}P\{^1H\}$ NMR in an NMR tube ($CDCl_3$, under purified N_2 or sealed under vacuum). Products are $[RuH(dcpe)_2]^+$ (**1**), $[RuCl(dcpe)_2]^+$ (**2**), dcpe oxide (**5**), $[Ru(\eta^2\text{-}O_2CR)(dcpe)_2]^+$ (R = Me, **6a**; Ph, **6b**; C_6H_{13}, **6c**), and $[RuCl(\eta^2\text{-}H_2)(dcpe)_2]^+$ (**7**). [b] Mole ratio of complex **4** to reagent. [c] Based on starting **4** (see also Experimental). [d] TEMPO added (1 : 1 mole ratio) to the reaction solution. [e] AIBN (1 : 1 mole ratio) as additive. [f] Based on starting PPh_3.

the definition by Collman and Otsuka (that is, the formal oxidation state of the metal does not change in the net oxygen-transfer reaction).[23] In the present case, the overall oxygen-transfer reaction from **4** to the substrate regenerates the O_2-activating species **1** without oxidation of the metal. To the best of our knowledge, such a reactivity is unprecedented for dioxygen complexes of the late transition metals, which generally react with aldehydes to give a carboxylato complex with the metal in an oxidized form.[1h,31,32] Thus, $[Ru(\eta^2\text{-}O_2)(CO)(CNR)(PPh_3)_2]$, formally a d^8 dioxygen complex, reacts with CH_3CHO to give the bis(carboxylato) d^6 complex $[Ru(\eta^1\text{-}O_2CMe)_2(CO)(CNR)(PPh_3)_2]$,[31a] whereas $[Pt(\eta^2\text{-}O_2)(PPh_3)_2]$ reacts with aldehydes forming the metallacycle $[Pt(O^1OC(R)(H)O^3\text{-}O^1,O^3)(PPh_3)_2]$[30b] or, in the presence of air, $[Pt(\eta^1\text{-}O_2CR)_2(PPh_3)_2]$.[31b]

In view of its nucleophilic character, **4** was also reacted with acids to check whether the dioxygen ligand is protonated. The reaction of **4** with CH_3CO_2H (1 : 1 molar ratio) gives the acetato complex $[Ru(\eta^2\text{-}O_2CCH_3)(dcpe)_2]^+$ (**6a**): after 1 h, 70% of **4** is converted to **6a** with 40% yield. The remaining **4** is probably converted to undetectable paramagnetic species (see Experimental). Protonation of **4** by $[Et_2OH]BF_4$ gives a complex mixture of non-hydridic Ru^{II} complexes. Both reactions indicate that the η^2-O_2 ligand is eliminated as O_2, not as H_2O_2. Thus, protonation apparently occurs at the hydride ligand rather than at η^2-O_2, and is followed by elimination of H_2.

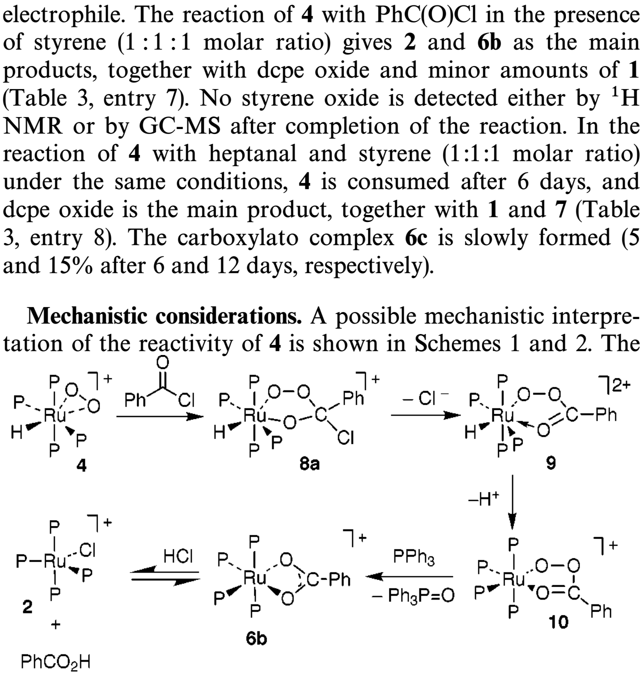
Co-oxidation reactions. The first attempts to exploit the oxygen-transfer reaction from **4** in the co-oxidation of a nucleophile (Nu) and an electrophile (El) (eqn. 1) were only partially successful.



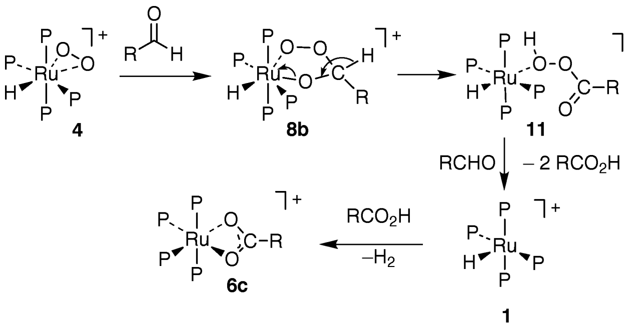
(1)

Oxygen transfer from **4** to PPh_3 and PhC(O)Cl (1 : 1 : 1 molar ratio) is moderately efficient, with 25% of starting PPh_3 converted into $Ph_3P{=}O$ after 5 days (Table 3, entry 6). The other reaction products are the carboxylato derivative $[Ru(\eta^2\text{-}O_2CPh)(dcpe)_2]^+$ (**6b**), **2**, and **1**. Partial oxidation of the diphosphine ligand occurs: some dcpe oxide **5** is observed. However, styrene is not epoxidized in the presence of **4** and an electrophile. The reaction of **4** with PhC(O)Cl in the presence of styrene (1 : 1 : 1 molar ratio) gives **2** and **6b** as the main products, together with dcpe oxide and minor amounts of **1** (Table 3, entry 7). No styrene oxide is detected either by ^1H NMR or by GC-MS after completion of the reaction. In the reaction of **4** with heptanal and styrene (1:1:1 molar ratio) under the same conditions, **4** is consumed after 6 days, and dcpe oxide is the main product, together with **1** and **7** (Table 3, entry 8). The carboxylato complex **6c** is slowly formed (5 and 15% after 6 and 12 days, respectively).

Mechanistic considerations. A possible mechanistic interpretation of the reactivity of **4** is shown in Schemes 1 and 2. The co-oxidation of PhC(O)Cl and PPh_3 by **4** can be explained with the generally accepted mechanism of electrophilic peroxidation (Scheme 1).[1f,g] The cyclic peroxymetallation reaction[1f] involves opening of the $M(\eta^2\text{-}O_2)$ ring, followed by nucleophilic attack of $M(\eta^1\text{-}O_2)$ onto the carbonyl C atom.[21b] Elimination of Cl^- from the peroxy metallacycle **8a** gives the ruthenium(IV) hydride **9**, which reductively eliminates H^+ as it must be very acidic.[33] Reaction of the peroxy intermediate **10** with PPh_3 before dissociation of RC(O)OOH takes place would explain why free RC(O)OOH is not detected. The platinum congener of **10** has been suggested as an intermediate in the analogous reaction involving $[Pt(\eta^2\text{-}O_2)(PPh_3)_2]$.[25b]



Scheme 1



Scheme 2

The reaction of **4** with heptanal differs from the previous one in that the formyl H atom can be reductively eliminated from **8b** instead of the hydride, which eventually gives the five-co-ordinate hydride **1** (Scheme 2). This would explain why oxygen transfer from **4** regenerates the O_2 binding species. The reaction of the peroxy acid with the second equivalent of RCHO can occur either directly or, more probably, with the mediation of the metal, for instance *via* formation of a highly reactive oxometal species from **11**. Support for this possibility comes from our recent observation that the related dioxygen complex $[OsCl(\eta^2\text{-}O_2)(dcpe)_2]^+$ forms the Os^{IV} oxo complex $[OsCl(O)(dcpe)_2]^+$.[34] A peculiar feature of the reactions of **4** with heptanal is the formation of considerable amounts of $[RuCl(\eta^2\text{-}H_2)(dcpe)_2]^+$ (**7**) (Table 3, entries 3, 8) along with **1**. Independent experiments show that **7** is not produced by reaction of **1** with CD_2Cl_2. We suggest that **7** is formed by protonation of the hydride in **1**, followed by abstraction of Cl^- from the solvent. The acidic species could be the RC(O)OOH moiety in **11**, since co-ordination to the metal enhances the acidity of the peroxy acid. Alternatively, protonation of unreacted **4**, followed by loss of O_2, can also produce **7**. The carboxylato derivative **6c** is eventually formed by reaction between heptanoic acid and **1**, as confirmed by independent experiments showing that $C_6H_{13}CO_2H$ reacts with **1** to form **6c**, probably *via* protonation of the hydride ligand and loss of H_2 from an undetected dihydrogen complex.

Finally, the presence of minor amounts of paramagnetic products, as well as the experiments with radical scavengers (TEMPO) and initiators (AIBN), leave the possibility open that more than one mechanism is operative. We can not exclude that the η^2-O_2 ligand abstracts the formylic H atom to give a $M^{III}OOH$ species.[35] A mechanism based on the elimination of HOO^- from **4**, analogous to that suggested for the catalytic oxidation of PPh_3 by $[Pt(\eta^2\text{-}O_2)(PPh_3)_2]$,[36] does not seem to apply here, since the hydride ligand is retained to give **1**.

Only a few $M(\eta^2\text{-}O_2)$ complexes are known to react *rapidly* with menadione.[21] This has been proposed as a diagnostic tool for the nucleophilicity of the η^2-O_2 moiety. In the case of **4**, the reaction is very slow (5 days), and complicated by the oxidative degradation of menadione and of its epoxide. Both reactions suggest that the C=C bond is oxidatively cleaved in the presence of **4**, a reaction already observed with ruthenium–O_2 systems.[13b] On the basis of the reactivity results, we suggest that **4** and [Pt(η^2-O_2)(PPh_3)$_2$] are nucleophiles of similar strength, since **4** reacts with RCHO and PhC(O)Cl, and only very slowly with menadione.[21a]

Concluding remarks

A weak agostic interaction between a cyclohexyl methylene group and ruthenium seems to contribute to the stabilization of the five-co-ordinate hydride $[RuH(dcpe)_2]^+$. Thus, steric factors alone do not explain the stability of the 16-electron complexes $[MX(P{-}P)_2]^+$ (M = Ru, Os) and their reactivity toward O_2 (and H_2). Electronic factors, such as weak agostic interactions and the σ- and π-donor/acceptor properties of the ligands, must be also considered in this context. In particular, the good donor properties of dcpe and hydride ligands are apparently responsible for the reactivity of **1** toward O_2. The resulting peroxo species **4** is a class II nucleophile, according to Valentine's definition, as it reacts with organic electrophiles such as TCNE, PhC(O)Cl, and RCHO. Of particular interest, **4** oxidizes RCHO to RC(O)OH, restoring the oxygen-binding species **1**. This scarcely documented "reductive" oxygen transfer to organic substrates opens the way to developing catalytic transformations. Our efforts are presently directed to getting a better insight into the mechanistic aspects of these reactions, and to enhancing the stability of the complex toward oxidative degradation of the diphosphine ligand.

Experimental

General

Manipulations involving solutions of the complexes were performed either under argon with use of Schlenk-line techniques or in a glove box (Braun) under purified nitrogen. Solvents were purified by standard methods. All chemicals used were of reagent grade or comparable purity. The ligand dcpe was purchased from Strem and $RuCl_3 \cdot H_2O$ from Aldrich; TCNE was sublimed twice before use. Complexes $\mathbf{1} \cdot BPh_4$,[3a] **3**,[10a] and $[RuH(Cl)(dcpe)_2]$[10a] were prepared as previously reported. Unless otherwise stated, yields are based on the metal. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer. Microanalyses were performed by the Laboratory of Microelemental Analysis at the Organic Laboratory at ETH. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were taken on a Bruker DPX 300 spectrometer. ^1H and $^{31}P\{^1H\}$ NMR chemical shifts (δ) are relative to TMS and 85% H_3PO_4, respectively. $^{13}C\{^1H\}$ NMR chemical shifts were internally referenced to solvent $CDCl_3$ (δ 77.0). Mass spectroscopy was carried out by the analytical service of the Organic Laboratories at the ETH Zürich.

Preparations and reactions

$[RuH(dcpe)_2]PF_6$, $\mathbf{1} \cdot PF_6$. $[RuH(Cl)(dcpe)_2]$ (200 mg, 0.20 mmol) was dissolved in CH_3OH (15 mL) and a CH_3OH solution (3 mL) of $TlPF_6$ (75 mg, 0.41 mmol) was added to the deep orange solution, from which orange microcrystals precipitated during 2 h. Cooling in ice, decanting the supernatant solution and drying in vacuum gave the crude product. Recrystallization from CH_2Cl_2–Pr^iOH yielded $\mathbf{1} \cdot PF_6$ (140 mg, 63%). Anal. Found: C, 56.94; H, 8.72. Calcd. for $C_{52}H_{97}F_6P_5Ru$: C, 57.18; H, 8.95%. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ −32.0 (Ru—*H*, qt, ^2J(PH) = 19.2 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 25 °C): δ 73.6 (s, 4 P), −144.3 (spt, PF_6, ^1J(PF) = 713 Hz).

$[RuH(\eta^2\text{-}O_2)(dcpe)_2]PF_6$, 4. Complex **1** (200 mg, 0.091 mmol) was dissolved in CH_2Cl_2 (4 mL) and stirred in air for 45 min. Evaporation of the solvent in vacuum gave brown microcrystals of **4** (124 mg, 60%), which were recrystallized from CH_2Cl_2–ethanol. ^1H and ^{31}P NMR data as for the $[BPh_4]^-$ analogue.[3a] UV/VIS (CH_2Cl_2) λ/nm (ε/mol L^{-1} cm^{-1}): 213(sh), 236 (750), 260 (1060), 280 (1052), 353 (530). Anal. Found: C, 55.29; H, 9.02. Calcd. for $C_{52}H_{97}O_2F_6P_5Ru$: C, 55.55; H, 8.69%. FAB^+ MS (NBA matrix): *m/z* 980 $[M]^+$, 12%; 964 $[M - O]^+$, 7%; 948 $[M - 2\ O]^+$, 100%; 864 $[M - O_2 - C_6H_{11}]^+$, 6%.

Reaction of 4 with TCNE. Complex **4** (100 mg, 0.088 mmol) and TCNE (12 mg, 0.088 mmol) were dissolved in CH_2Cl_2 and stirred for 2 h. The solution turned first green-blue, then brown-black. Pumping the solvent off resulted in a brown-black powder. Recrystallization from different solvent mixtures gave intractable oils. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 2.4–0.4 (CH_2). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 25 °C): δ 70.4 (s), −144.3 (spt, PF_6, ^1J(PF) = 713 Hz). IR (KBr): 2209s, 2120m, 2098m, 1611s, 1327m, ν(P–F) 841vs cm^{-1}. FAB^+ MS (NBA matrix): *m/z* 1005, 9%; 973, 21%.

Reactions of 4 in an NMR tube. Complex **4** (20 mg, 18 μmol) and the appropriate reagent were dissolved in CD_2Cl_2 (0.5 mL) in an NMR tube under argon: (*a*) menadione (3 mg, 18 μmol); (*b*) acid-free $C_6H_{13}CHO$ (5 μl, 36 μmol), (*c*) PPh_3 (5 mg, 18 μmol) and acid-free PhC(O)Cl (2 μl, 18 μmol); (*d*) styrene (2 μl, 18 mmol) and acid-free PhC(O)Cl (2 μl, 18 μmol), (*e*) styrene (2 μl, 18 μmol) and acid-free $C_6H_{13}CHO$ (2 μl, 18 μmol). The reaction solution was degassed by three freeze-thaw-pump cycles, and then the NMR tube was sealed under vacuum. Alternatively, the solutions were prepared in glove box, and the tube closed under N_2. The progress of the reactions was monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopies, using the ^{31}P NMR resonance of $[PF_6]^-$ as internal reference. This is justified by the similarity of the relaxation times and by the chemical stability of the anion under these conditions. The total amount of the Ru containing products is generally below 100% since most reactions yield variable amounts of paramagnetic by-products, depending on the substrate. Most of these yet unidentified species give a characteristic high-field ^1H NMR pattern in the δ region between 0 and −4, but cannot be quantified as they are ^{31}P NMR silent. In some cases, the presence of several products with complicated ^{31}P spectral patterns in small amounts hinders accurate integration of the spectra. The percentage of dcpe oxide is not normalized to starting **4**. After the reaction, the volatile products were analysed by GC-MS.

$[Ru(\eta^2\text{-}O_2CCH_3)(dcpe)_2]PF_6$, 6a. Complex **3** (100 mg, 0.098 mmol) was dissolved in benzene (5 mL) and $Tl[PF_6]$ (69 mg, 0.20 mmol) was added to the yellow-orange solution. After stirring the resulting violet solution for 45 min, a MeOH solution (1 mL) of $NEt_4(O_2CCH_3)$ (15 mg, 0.20 mmol) was added. The solution turned yellow within 20 min, after which the solvent was evaporated in vacuum and the residue was dissolved in CH_2Cl_2. After filtration over Celite, addition of MeOH (6 mL) and evaporation of CH_2Cl_2, followed by addition of ether (8 mL), gave **6a** (51 mg, 45%) as a yellow precipitate, which was filtered off and dried in vacuum. Anal. Found: C, 51.40; H, 7.90. Calcd. for $C_{54}H_{99}F_6O_2P_5Ru \cdot 2\ CH_2Cl_2$: C, 50.95; H, 7.86%. IR (KBr): ν_{asym}(OCO) 1559s, ν_{sym}(OCO) 1456s, η(P—F) 848vs cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.4–0.4 (CH_2 + CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 °C): AA′XX′, δ 53.2 (t, ^2J(PP′) = 16.4 Hz), 71.4 (t), −144.3 (spt, PF_6, ^1J(PF) = 713 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 185.3 (s, CH_3CO_2), 53.1 (s, CH_3CO_2), 45–17 (aliphatic CH_2). FAB^+ MS (NBA matrix): *m/z* 1006 $[M]^+$, 100%; 922 $[M - Cy]^+$, 10%.

$[Ru(\eta^2\text{-}O_2CC_6H_5)(dcpe)_2]PF_6$, 6b. Complex **6b** (73 mg, 63%) was prepared from $C_6H_5CO_2H$ (24 mg, 0.20 mmol) and NEt_3 (27 μL, 0.20 mmol) as described for **6a**. Anal. Found: C, 58.28; H, 8.66. Calcd. for $C_{59}H_{109}O_2F_6P_5Ru$: C, 58.45; H, 8.40%. IR (KBr): ν_{asym}(OCO) 1522s, ν_{sym}(OCO) 1497s, ν(P—F) 848vs cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.4–7.9 (C_6H_5), 2.4–0.4 (CH_2). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 °C): AA′XX′, δ 54.8 (t, $^2J(PP') = 16.4$ Hz), 73.4 (t), −144.3 (spt, PF_6, $^1J(PF) = 713$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 180.0 (s, RCOO), 132.1, 131.7, 127.9, 127.3 (s, C_6H_5), 48–18 (aliphatic CH_2 and CH_3). FAB$^+$ MS (NBA matrix): m/z 1068 $[M]^+$, 100%; 984 $[M - Cy]^+$, 17%; 644 $[M - dcpe - H]^+$, 6%.

$[Ru(\eta^2\text{-}O_2CC_6H_{13})(dcpe)_2]PF_6$, 6c. Complex **6c** was prepared from heptanoic acid (28 μL, 0.20 mmol) and NEt_3 (27 μL, 0.20 mmol) as described for **6a**. Recrystallization from benzene–ether gives **6c** (81.3 mg, 67%) as a yellow crystalline solid. IR (KBr): ν_{asym}(OCO) 1526s, ν_{sym}(OCO) 1453s, ν(P—F) 837vs cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.4–2.4 (CH_2). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 °C): δ AA′XX′, 52.4 (t, $^2J(PP') = 16.4$ Hz), 70.5 (t), −144.3 (spt, PF_6, $^1J(PF) = 713$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 188.1 (s, RCOO), 46–13.9 (aliphatic CH_2 and CH_3). FAB$^+$ MS (NBA matrix): m/z 1076 $[M]^+$, 100%; 993 $[M - Cy]^+$, 23%; 945 $[M - C_7H_{13}O_2 - 2\,H]^+$, 6%.

Crystallography

$[RuH(dcpe)_2]PF_6$, $1\cdot PF_6$. Dark red crystals of $1\cdot PF_6$, suitable for X-ray analysis, were grown from CH_2Cl_2–Pr^iOH in a glove box under purified N_2. A prism (0.30 × 0.25 × 0.20 mm) was mounted in a 0.5 mm glass capillary in glove box. Crystal data for $C_{52}H_{97}F_6P_5Ru$, **1**: $M = 1092.22$, monoclinic, $P2/c$ (No 13), $a = 19.692(1)$, $b = 12.494(1)$, $c = 22.413(2)$ Å, $\beta = 95.960(7)°$, $U = 5467.0(7)$ Å^3, $Z = 4$, $D_c = 1.327$ Mg m^{-3}, μ(Mo-Kα) = 0.487 mm^{-1}, $F(000) = 2328$, $T = 298$ K, λ(Mo-Kα) = 0.71073 Å. The data were collected on a STOE IPDS (image plate detector system) in the 2θ range 5.0–50.0° (oscillation, 6 min exposure time, 181 images). Unit cell dimensions determination and data reduction were performed by standard procedures,[37] and an additional absorption correction using ABSCOR, including all non-hydrogen atoms, was applied. The structure was solved with SHELXTL PLUS[38] using direct methods. Of the 30 551 measured reflections with index ranges $-22 \leqslant h \leqslant 20$, $-14 \leqslant k \leqslant 14$, $-25 \leqslant l \leqslant 25$, 8503 were independent ($R_{int} = 0.0581$), and 5983 with $|F|^2 > 2\sigma(|F|^2)$ were used in the refinement. A total of 867 parameters were refined by full-matrix least squares using SHELXS-96[39] [data-to-parameter ratio 1 : 7, quantity minimized $\Sigma w(|F_o|^2 - |F_c|^2)^2$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $3P = F_o^2(\geqslant 0) + 2F_c^2$] with anisotropic displacement parameters for all non-H atoms. All hydrogen atoms other than the hydride were located in the Fourier peak list and refined with fixed isotropic parameters ($U_{iso} = 0.080$ Å^2). Molecular graphics were drawn with ORTEP II[38] with 50% ellipsoids. Final residuals were $R = 0.0457$ and $wR = 0.0993$ (obs. data), and $R = 0.0787$ and $wR = 0.1088$ (all data), GOF 0.995. (N.B.: wR values are calculated on $|F|^2$, see Supplementary material). Maximum and minimum difference peaks were +0.96 and −0.29 e Å^{-3}, largest and mean $\Delta/\sigma = -0.001$ and 0.000.

***trans*-$[RuCl_2(dcpe)_2]$, 3.** A pale orange cube of **3**, grown from CH_2Cl_2–acetone, was mounted on a glass capillary. Crystal data for $C_{52}H_{96}P_4Ru\cdot 2CH_2Cl_2$: $M = 1187.0$, monoclinic, space group $P2_1/n$, cell dimensions (293 K) $a = 13.256(2)$, $b = 16.259(4)$, $c = 14.189(4)$ Å, $\beta = 100.05(2)°$, $U = 3011.2(12)$ Å^3, $Z = 2$, $D_c = 1.309$ Mg m^{-3}, μ(Mo-Kα) = 6.66 cm^{-1} (graphite monochromated), $\lambda = 0.710\,73$ Å, $F(000) = 1260$. The data were collected on a Syntex $P2_1$ diffractometer using the ω scan mode (2θ range = 3.0–40.0°) with variable scan speeds (1.0–4.0° min^{-1} in ω) to ensure constant statistical precision on the collected intensities. One standard reflection was measured every 120 reflections; no significant variation was detected. A face-indexed numerical absorption correction was applied. The structure was solved using Patterson methods. Of the 2824 independent reflections with index ranges $0 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 15$, $-13 \leqslant l \leqslant 13$, 2178 with $F > 4.0\sigma(F)$ were used in the refinement. A total of 296 parameters were refined by full-matrix least squares using SHELXTL PLUS[38] [data-to-parameter ratio 7.4 : 1, quantity minimized $\Sigma w(F_o - F_c)^2$] with anisotropic displacement parameters for all non-H atoms. The contribution of the H atoms in idealized positions (riding model with fixed isotropic $U = 0.080$ Å^2) was taken into account but not refined. Two independent CH_2Cl_2 molecules were located in the final Fourier map. Final residuals were $R = 0.039$ and $wR = 0.055$ (obs. data), and $R = 0.050$ and $wR = 0.058$ (all data), GOF 0.98 (weighting scheme $w^{-1} = \sigma^2(F) + 0.0021F^2$). Maximum and minimum difference peaks were +0.54 and −0.61 e Å^{-3}, largest and mean $\Delta/\sigma = 0.040$ and 0.002. Selected interatomic distances and angles are reported on Fig 2.

CCDC reference number 440/088. See http://www.rsc.org/suppdata/nj/1999/199/ for crystallographic files in .cif format

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