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Synthesis and characterization of new ruthenium(II) complexes containing diisopropylmethylphosphine

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The reaction between $RuCl_3$ and P^iPr_2Me in 2-methoxyethanol yielded the five-co-ordinate complex $[RuCl_2(CO)(P^iPr_2Me)_2]$ in which the phosphine groups show a *cisoid* arrangement. The co-ordination sphere of the ruthenium nucleus can be completed with neutral ligands such as CO, ^tBuNC, Hpz, 3,5-dimethylpyrazole and $HN{=}CPh_2$. Likewise, it reacts with S-donor reagents like PhSH and 2-sulfanylpyridine and readily undergoes metathesis reactions with salts of some chelating ligands like NaS_2CNEt_2, KS_2COR (R = Me, Et or ^iPr) and K(acac) which are bonded in a bidentate mode.

Introduction

The interest in the synthesis and characterization of new co-ordinatively unsaturated transition-metal complexes arises because they represent very reactive intermediates in many catalytically operating processes [1,2] and provide transition-metal sites for the binding and activation of small molecules.[3] The use of innovative auxiliary ligands gives rise to new complexes related to others previously known but with the possibility of new features and new ways to the understanding of these sort of processes.[4] Bulky phosphine ligands are one of the most commonly employed. They are implicated in many different processes of co-ordination and catalytic chemistry,[2] and a small steric modification of a phosphine ligand can dramatically alter the reactivity of a complex.[5] In this context, a family of five-co-ordinate complexes of general formula $[MH(Cl)(CO)(PR_3)_2]$ have been the subject of extensive analysis. The bulkiness and the donating power of the phosphine are decisive in hydride formation and in the stabilization of co-ordinatively unsaturated species. Phosphine ligands like PCy_3, P^iPr_3 or P^tBu_2R (R = Me or Et) are able to stabilize 16-electron complexes from $RuCl_3$ in primary alcohols.[6] A considerable part of these investigations has grown up around the complexes $[MH(Cl)(CO)(P^iPr_3)_2]$ (M = Ru or Os) and their derivatives,[7] which have exhibited a rich chemistry and catalytic activity.[1] However, saturated compounds like $[RuH(Cl)(CO)(PPh_3)_3]$ are frequently employed as starting materials and catalysts.[8] The complex $[RuCl_2(CO)_2(PEt_3)_2]$ was used in the synthesis of a series of ruthenium(II) bis(acetylides) and bis(diacetylides).[9] Similar complexes with triisopropylstibine have recently been obtained, also using $RuCl_3$, affording the saturated but reactive compounds $[RuCl_2(CO)(Sb^iPr_3)_3]$ and $[RuH(Cl)(CO)(Sb^iPr_3)_3]$.[4]

We have used diisopropylmethylphosphine as a new ligand in the synthesis of new organometallic complexes. In addition to its own electronic and steric characteristics, this phosphine may, similarly to P^tBu_2Me, respond to the steric demands involved during reactions like adduct formation.[5a] We are interested in the synthesis of new unsaturated complexes and their reactivity towards mono- and bi-dentate ligands, potentially N-, C-, O- and S-donors.

Results and discussion

Synthesis and structural characterization of the starting material

In this paper we describe the synthesis and characterization of a new 16-electron complex containing diisopropylmethylphosphine. On the basis of analogous reactions with different phosphines [6] we attempted to obtain a good starting material with the new phosphine and were first interested in the possibility of synthesis of the hypothetical *transoid* complex $[RuH(Cl)(CO)(P^iPr_2Me)_2]$. However, the interaction of ruthenium trichloride in 2-methoxyethanol with three equivalents of the phosphine P^iPr_2Me, heated under reflux for 24 h, yields the unexpected but also unsaturated complex $[RuCl_2(CO)(P^iPr_2Me)_2]$ **1** instead of the hydridochloride compound, as a yellow solid with a yield of 70–90%. This complex shows a *cisoid* arrangement between the phosphine ligands, displaying two doublet resonances in the ^{31}P-{^1H} NMR spectrum with a P–P′ coupling constant of 23.2 Hz. No fluxional processes have been observed at high or low temperatures. The arrangement of the phosphines and the impossibility of giving rise to the hydride formation are the main structural differences with analogous complexes with the related ligands P^iPr_3 and P^tBu_2Me, both bulkier and probably stronger donors.

The lack of suitable crystals of compound **1** for X-ray diffraction prevents us from determining whether this complex is trigonal bipyramidal or square pyramidal. However, the proposed structures for species like $[RuH(Cl)(CO)L_2]$ (L = P^iPr_3,[6a] P^tBu_2Me [6b] or Cy [6c]), $[RuCl_2(CO)L_2]$ (L = PCy_3 [6d] or P^tBu_2Me [6e]), and the stereochemistry of the adducts, make a square pyramidal geometry the most plausible. In agreement with Caulton and co-workers [10] regarding π stabilization of unsaturation in $[RuH(X)(CO)(P^tBu_2Me)_2]$, we propose a *transoid* arrangement between the carbonyl and one of the chloride ligands, delocalizing π donation by Cl. This hypothesis, in addition to the non-equivalence of the phosphorus nuclei, places one phosphine ligand *trans* to the vacant co-ordination site. In support of this we note Δδ (Table 1) in the ^{31}P-{^1H} NMR spectrum of complex **1** in comparison to those of the adducts $[RuCl_2(CO)(L)(P^iPr_2Me)_2]$, which, maintaining the AB coupling pattern in their ^{31}P-{^1H} NMR spectra, show a different variation of δ for the phosphorus nuclei and a major influence of the incoming ligand upon the phosphine *trans* to the vacant site. Finally, the carbonyl group in compound **1** displays a triplet resonance in the ^{13}C-{^1H} NMR spectrum, which is in accord with its disposition *cis* to both phosphine ligands. This arrangement of the ligands is in contrast with those of the related $[RuCl_2(CO)L_2]$ (L = PCy_3 [6d] or P^tBu_2Me [6e]) in which the apical position is occupied by the carbonyl group.

Table 1 Chemical shifts, δ, of the ^{31}P NMR signals, for complexes showing a AB coupling pattern

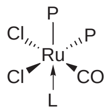
Compound	L		δ P	δ P′	$\Delta\delta$
1	—		45.4	44.2	1.2
2	CO		40.5	15.2	25.3
3a	^{t}BuNC		40.8	16.4	24.4
4	$HNCPh_2$		37.0	31.9	5.1
5	Hpz		36.2	34.2	2.0
6	3,5-Me_2Hpz		35.7	32.5	3.2
8a	2-PySH		37.2	28.7	8.5

Table 2 Selected bond distances (Å) and angles (°) for compound [$RuCl_2$(CO)(NH=CPh_2)(P^iPr_2Me)$_2$]. E.s.d.'s are in parenthesis.

Ru(1)–Cl(1)	2.481(2)	Ru(1)–C(1)	1.800(7)
Ru(1)–Cl(2)	2.458(2)	O(1)–C(1)	1.167(7)
Ru(1)–P(1)	2.373(2)	N(1)–C(2)	1.296(7)
Ru(1)–P(2)	2.371(2)	C(2)–C(3)	1.469(9)
Ru(1)–N(1)	2.144(5)	C(2)–C(9)	1.480(9)
Cl(1)–Ru(1)–Cl(2)	85.44(6)	P(1)–Ru(1)–N(1)	87.8(1)
Cl(1)–Ru(1)–P(1)	86.69(6)	P(1)–Ru(1)–C(1)	92.8(2)
Cl(1)–Ru(1)–P(2)	94.82(6)	P(2)–Ru(1)–N(1)	165.1(1)
Cl(1)–Ru(1)–N(1)	79.5(1)	P(2)–Ru(1)–C(1)	87.7(2)
Cl(1)–Ru(1)–C(1)	177.5(2)	N(1)–Ru(1)–C(1)	98.0(2)
Cl(2)–Ru(1)–P(1)	169.29(6)	Ru(1)–N(1)–C(2)	143.6(4)
Cl(2)–Ru(1)–P(2)	82.23(6)	Ru(1)–C(1)–O(1)	176.8(6)
Cl(2)–Ru(1)–N(1)	83.6(1)	N(1)–C(2)–C(3)	119.9(6)
Cl(2)–Ru(1)–C(1)	94.7(2)	N(1)–C(2)–C(9)	121.3(5)
P(1)–Ru(1)–P(2)	105.70(6)	C(3)–C(2)–C(9)	118.7(5)

Reactions with CO and ^{t}BuNC

The unsaturated character of complex **1** is evidenced by the easy incorporation of neutral ligands in the co-ordination sphere of the ruthenium. When carbon monoxide is bubbled through a CH_2Cl_2 solution of **1** the colour rapidly changes from yellow to colourless. The dicarbonyl complex [$RuCl_2(CO)_2$-(P^iPr_2Me)$_2$] **2** is isolated as a white microcrystalline solid. Two intense absorptions appear at 1979 and 2053 cm^{-1} in the IR spectrum and the phosphorus nuclei show a two doublet pattern in the ^{31}P-{^{1}H} NMR spectrum. These data are consistent with an all *cis* disposition around the ruthenium atom, in contrast with that in the related complexes *cis,cis,trans*-[$RuCl_2(CO)_2(P^iPr_3)_2$],[11] all-*trans*-[$RuCl_2(CO)_2(L)_2$] (L = P^tBu_2-Me[6e] or PEt_3[9]) and also with *cis,trans*-[RuH(Cl)$(CO)_2L_2$] (L = P^iPr_3,[6a] P^tBu_2Me[6b] or PCy_3[12]), all of which show a *trans* phosphine arrangement. We note that even phosphines with less steric requirements like PPh_3 or PEt_3 prefer to form complexes maintaining a relative *trans* configuration.[8,9]

Treatment of complex **1** with *tert*-butyl isocyanide in THF gives the corresponding adduct **3a** as a white solid in good yield, and spectroscopically very similar to **2**. However, if this reaction is carried out in CH_2Cl_2 the resulting white solid **3b** exhibits only a singlet resonance in the ^{31}P-{^{1}H} NMR spectrum. The ^{13}C-{^{1}H} NMR resonance of the carbonyl group appears as a low field triplet for both **3a** and **3b**, confirming the presence of the two phosphines. This behaviour is not observed in the formation of the dicarbonyl complex **2**. The reason for this must involve the better σ-donor character of the isocyanide, allowing the rearrangement of the complex to a disposition in which the phosphine ligands become magnetically equivalent. The distinction between *cis*- or *trans*-phosphines only may be made from the coupling pattern of the methyl groups P^iPr_2*Me* in the ^{13}C-{^{1}H} NMR spectrum, which instead of the virtual triplet expected for a *trans*-diphosphine shows a multiplet centred at δ 6.1 for **3b**. This pattern is also observed with other complexes described later.

Reactions with N-donor ligands

Complex **1** readily forms adduct complexes with N-donor ligands like pyrazole, 3,5-dimethylpyrazole and even with diphenylmethanimine despite the weak nucleophilic character of the N atom in imine derivatives.[13] Thereby, the treatment of **1** with a slight excess of these reagents yielded the corresponding *cis*-diphosphine adducts [$RuCl_2$(CO)(L)(P^iPr_2Me)$_2$] (L = $NHCPh_2$ **4**, Hpz **5** or 3,5-Me_2Hpz **6**); each one shows in the IR spectra the ν(N–H) absorption between 3200 and 3300 cm^{-1}. The pyrazole derivatives **5** and **6** show a double ν(N–H) band due to the possibility of the existence of N-H···Cl interactions with the neighbouring chlorides.[11,14] Complexes **4**–**6** show in the ^{1}H NMR spectra at low field the corresponding signal for the NH proton, as a broad singlet.

Crystal structure of complex [$RuCl_2$(CO)(NH=CPh_2)-(P^iPr_2Me)$_2$] 4

Diphenylmethanimine reacts with complex **1** quickly and cleanly, yielding a yellow microcrystalline solid which when recrystallized from 1 : 1 CH_2Cl_2–Et_2O gave suitable crystals for X-ray diffraction (Fig. 1). This structure confirms some of our hypothesis about the disposition of the ligands in the parent complex **1.** The co-ordination geometry around the ruthenium atom can be described as a distorted octahedron with the two phosphorus atoms of the diisopropylmethylphosphine ligands in *cis* positions and the two chlorine atoms also occupying *cis* positions. The carbonyl ligand is *trans* in relation to one of the chloride ligands and if its direction is defined as axial the perpendicular plane is formed by two phosphorus, the other chlorine and the nitrogen atom which is in *trans* relation to one phosphorus. The π electronic influences can explain the fact that the best π acceptor is opposite to the best π-donor ligand. All distances and angles around ruthenium are in the normal range (Table 2). The P(1)–Ru(1)–P(2) angle is 105.70(6)° because of the steric demand of the bulky monodentate phosphine substituents. The distance Ru(1)–N(1) 2.144(5) Å is typical for a Ru–N single bond and is also similar to Os–N distances previously found in osmium imine complexes.[16] Angles around N(1) and C(2) show that both have sp^2 character, Ru(1)–N(1)–C(2) 143.6(4)° being bigger than the ideal 120° because of the smaller size of the hydrogen atom.

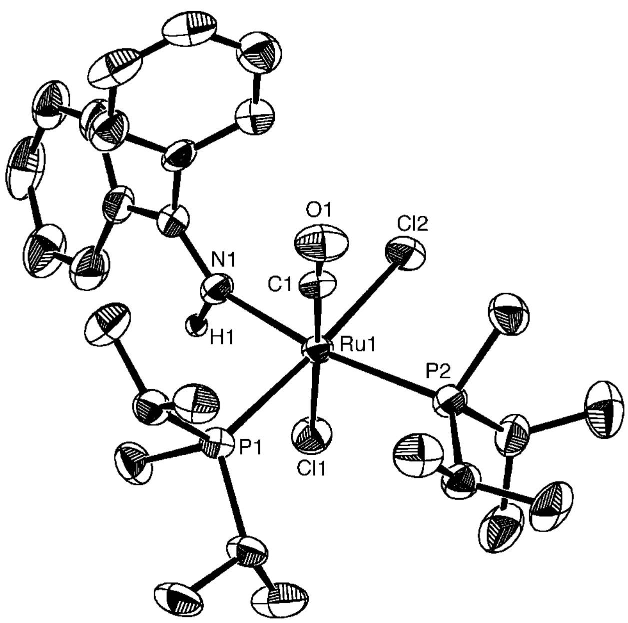


Fig. 1 An ORTEP[15] drawing of the compound [$RuCl_2$(CO)($NHCPh_2$)-(P^iPr_2Me)$_2$] **4**.

Reactions with benzenethiol and 2-sulfanylpyridine

Research into the chemistry of sulfur compounds has identified many modes of co-ordination and the reactivity pattern of their complexes.[17] Co-ordination complexes of neutral thiols are relatively uncommon presumably because of the high acidity of the SH functionality.[18] Complex **1** reacts immediately with benzenethiol affording a clear change from yellow to green, but not leading to a simple co-ordination of the neutral ligand. Evidence for the deprotonated nature of the ligand comes from the non-observation of the band *ν*(SH) near 2500 cm^{-1} in the IR spectrum, nor the corresponding ^1H NMR signal for the proton of co-ordinated thiol. The ^1H NMR spectrum shows broad signals corresponding to the protons of the phenyl ring of the thiophenolate ligand. Similar behaviour has been found for the five-co-ordinate thiolate complex $[Ru(SPh)(dippe)_2][BPh_4]$[19] (dippe = $^iPr_2PCH_2CH_2P^iPr_2$) and thiolate-bridged complexes.[20] Thereby, the result of the direct interaction of complex **1** with benzenethiol is the elimination of HCl in polar solvents to give the product **7**, but its mono- or binuclear nature cannot be distinguished only by NMR data. The IR spectrum shows the *ν*(CO) absorption split into two peaks, which seems to support the existence of a binuclear species with thiolate or chloride bridges. The definitive proof comes from mass spectrometry, which shows two peaks of the same intensity corresponding to the fragments $[M - PhS]^+$ and $[M - Cl]^+$, where the molecular weight of M matches exactly with a binuclear mixed-bridge complex $[\{RuCl(CO)(P^iPr_2Me)_2\}_2$-(μ-Cl)(μ-SPh)] **7**. The broadness of the signals in the ^1H NMR spectrum may be interpreted in terms of inversion at the pyramidal bridging sulfur atom.[20]

In contrast with this, the reaction of complex **1** with 2-sulfanylpyridine (PySH) affords the mononuclear product of addition $[RuCl_2(CO)(PySH)(P^iPr_2Me)_2]$ **8** as a mixture of the isomeric complexes **8a** and **8b**. When the **8a/8b** mixture is left in methylene chloride the concentration of **8a** decreases till disappearance, and **8b** becomes the only product. Monitoring the reaction by $^{31}P\text{-}\{^1H\}$ NMR at room temperature reveals the initial formation of a two doublets resonance corresponding to a *cis* disposition of the phosphines, which immediately decreases giving rise to a singlet at δ 27.8, indicating that **8a** and **8b** are the kinetic and thermodynamic reaction products, respectively. This singlet corresponds to the presence of two equivalent phosphines. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **8b**, the carbonyl ligand gives rise to a triplet signal at δ 200.3 with $^2J_{CP}$ = 14 Hz. The distinction between magnetically equivalent *cis*- or *trans*-phosphines is related to that in complex **3b**, because both compounds exhibit identical patterns for the $P^iPr_2\mathit{Me}$ carbon atom. The IR spectra of **8a** and **8b** show a weak band near 3200 cm^{-1} instead of *ν*(SH). This band is consistent with the presence of broad resonances at δ 14.4 and 14.8 respectively, in their ^1H NMR spectra, attributable to nitrogen-bound protons, which suggests that PySH exists as its 1*H*-pyridine-2-thione tautomeric form in this complex. This tautomeric process in 2-sulfanylpyridine is well established[21] and shows that the thione co-ordinates exclusively *via* the S atom, in contrast with the thiolate, which can adopt a variety of co-ordination modes. Recently, we have found the same co-ordination mode of PySH in $[RuCp(P^iPr_2Me)(PPh_3)(PySH)]$-$[BPh_4]$ and other related complexes.[22]

Metathesis reactions with bidentate ligands

Metathesis reactions of complex **1** with salts of diethyldithiocarbamate and *o*-alkyl dithiocarbonates afforded the neutral chelate complexes $[RuCl(\eta^2\text{-}S_2CNEt_2)(CO)(P^iPr_2Me)_2]$ **9** and $[RuCl(\eta^2\text{-}S_2COR)(CO)(P^iPr_2Me)_2]$ (R = Me **10**, Et **11** or ^{i}Pr **12**). Our recent study on these bidentate ligands showed the possibility of η^1 or η^2 co-ordination depending on the particular complex,[22] but in this instance the presence of a vacant co-ordination site and two metathetically exchangeable chloride ligands next to it makes η^2 co-ordination the most favourable process. This reaction takes place with a very high yield even under moderate conditions in a few hours, and the replacement

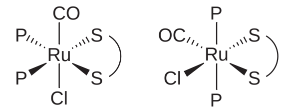


Fig. 2 Possible configurations for complex **9** maintaining phosphine ligands magnetically equivalent.

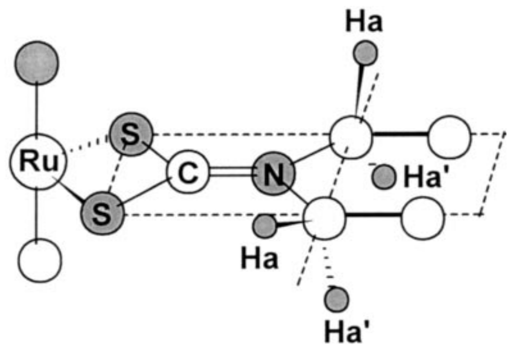


Fig. 3 The protons Ha and Ha′ become magnetically non-equivalent because the indicated plane is not a plane of symmetry of the molecule.

of the chloride is selective, affording only one of the two possible isomeric products.

In all cases, one singlet is observed in the $^{31}P\text{-}\{^1H\}$ NMR spectra, corresponding to two equivalent phosphines because of the triplet resonance of the carbonyl group in the $^{13}C\text{-}\{^1H\}$ NMR spectra, which indicates a *cis* arrangement with the two phosphine ligands. The unequivocal distinction between *cis*- or *trans*-phosphine disposition could be accomplished from the full interpretation of the ^1H, COSY, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectra of the diethyldithiocarbamate complex **9** (Fig. 2). The ethyl groups exhibit in the ^1H NMR spectrum a triplet signal for the methyl, whereas the methylene signal is split into two multiplets. Since the two ethyl groups proved to be equivalent in the $^{13}C\text{-}\{^1H\}$ NMR spectrum, showing only two singlet resonances, the duplicity of the methylene signals in the ^1H NMR spectrum only can be explained by the non-equivalence of the diastereotopic methylene protons.[17a] The C–N bond in the η^2-dithiocarbamate ligand is not single, *ν*(C=N) 1505 cm^{-1} in the IR spectrum, maintaining the adjacent atoms in the same plane (Fig. 3). This plane is not a plane of symmetry of the molecule, resulting in the non-equivalence of the methylene protons. We propose for this compound a structure with the group S_2P_2 disposed in the equatorial plane, which is the unique arrangement consistent with these spectral data.

Dithiocarbonate complexes **10–12** gave spectral data and patterns almost identical to those of the dithiocarbamate compound, with slight variations in δ attributable to their different donor character, and with the reasonable differences due to the diverse O-bonded alkyl groups. The most obvious divergence corresponds to the more electropositive $RO\mathit{C}S_2$ carbon atom of the dithiocarbonates which appears as a singlet near δ 230, while the analogous $Et_2N\mathit{C}S_2$ in dithiocarbamate appears at δ 211, in the $^{13}C\text{-}\{^1H\}$ NMR spectra. In this case, no irregularities in the ^1H NMR spectrum of the dithiocarbonate derivatives have been observed for the resonances corresponding to the alkyl groups.

All the complexes showing singlet resonances in their $^{31}P\text{-}\{^1H\}$ NMR spectra (**3b**, **8b** and **9–12**) display identical coupling patterns in the $^{13}C\text{-}\{^1H\}$ NMR spectra for the carbons directly bonded to the phosphorus atom. The spectral data of **3b** and **8b** do not allow one to decide if the mutual disposition of the phosphines is *cis* or *trans*, but on the basis of this similitude we propose a magnetically equivalent *cis* configuration.

The ruthenium complex **1** reacts with potassium acetylacetonate in CH_2Cl_2 to afford the corresponding β-diketonato complex $[RuCl(acac)(CO)(P^iPr_2Me)_2]$ **13**. The IR spectrum shows the presence of two *ν*(CO) bands at 1520 and 1590 cm^{-1} assign-

Table 3 Summary of crystal data and crystal structure analysis for compound $[RuCl_2(CO)(NH{=}CPh_2)(P^iPr_2Me)_2]$

Chemical formula	$C_{28}H_{45}Cl_2NOP_2Ru$
M	645.59
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	9.204(4)
b/Å	17.129(4)
c/Å	10.041(4)
β/°	104.65(3)
V/Å^3	1531.4(9)
T/K	290.2
Z	2
μ(Mo-Kα)/cm^{-1}	8.01
Unique reflections	2915 (R_{int} = 0.143)
Observed reflections ($I > 3\sigma$)	2452
R	0.0289
R′	0.0353

able to bidentate O-bonded acac.[23] The ^{1}H NMR spectrum exhibits two methyl resonances of equal intensity at δ 1.90 and 1.95, and the ^{13}C-{^{1}H} NMR spectrum displays two signals for the methyl carbons and two for the ketonic carbons, indicative of chelate acac bound *trans* to an asymmetric ligand pair, in accord with the data observed for the analogous complex $[RuCl(acac)(CO)(PPh_3)_2]$.[24] The ^{31}P-{^{1}H} NMR spectrum consists of two doublet resonances, in contrast with the chelate complexes **9**–**12**. These data allow one to conclude that this metathesis reaction leads to selective substitution of the other chloride group of the complex, showing a different preference between S- and O-donor ligands.

Experimental

General procedures

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk techniques. The solvents THF, Et_2O, and light petroleum (boiling point range 40–60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. The compound P^iPr_2Me was obtained by reaction of P^iPr_2Cl (Aldrich) with MgMeI in Et_2O. The IR spectra were recorded in Nujol mulls on a Perkin-Elmer FTIR Spectrum 1000 spectrophotometer, NMR spectra on Varian Unity 400 MHz or Varian Gemini 200 MHz spectrometers. Chemical shifts are given in ppm from $SiMe_4$ (^{1}H and ^{13}C-{^{1}H}) or 85% H_3PO_4 (^{31}P-{^{1}H}). Microanalyses were performed by the Serveis Científico-Tècnics, Universitat of Barcelona. Electrospray ionization mass spectrometry (ESI-MS) was performed on a VG Platform single-quadrupole mass spectrometer (Micromass Instruments, Altrincham, UK) equipped with an electrospray ionization source, operating in the positive-ion mode at a probe tip voltage of +3.5 kV. The extraction cone voltage was varied from +35 to −35 V.

Structure determination of $[RuCl_2(CO)(NH{=}CPh_2)(P^iPr_2Me)_2]$ 4

Details are given in Table 3. Data collection was carried out using an AFC6S-Rigaku automatic diffractometer in the ω–2θ scan mode with monochromated Mo-Kα radiation. The structure was solved by Patterson methods and subsequent expansion of the models using DIRDIF.[25] Reflections having $I > 3\sigma(I)$ were used for structure refinement. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were included at idealized positions and not refined. Since the space group is non-centrosymmetric both enantiomorphs were checked and no significant differences found between them. All calculations for data reduction, structure solution, and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN[26] software system and ORTEP[15] for plotting.

CCDC reference number 186/1484.

See http://www.rsc.org/suppdata/dt/1999/2399/ for crystallographic files in .cif format.

Preparations

$[RuCl_2(CO)(P^iPr_2Me)_2]$ 1. To a solution of $RuCl_3{\cdot}xH_2O$ (0.50 g, 2.5 mmol) in 2-methoxyethanol (10 ml) was added the phosphine P^iPr_2Me (1.2 ml, 8 mmol). The resulting mixture was heated under reflux with continuous stirring for 24 h. After removing the solvent under reduced pressure, ethanol (10 ml) and light petroleum (10 ml) were added to the residue, yielding the precipitation of a yellow solid, which was filtered off, washed with light petroleum and acetone, and dried under vacuum. Yield: 1 g (86%). Calc. $C_{15}H_{34}Cl_2OP_2Ru$: C, 38.8; H, 7.32. Found: C, 39.1; H, 7.27%. IR (Nujol, cm^{-1}): ν(CO) 1939. ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ 1.18–1.37 (m, 24 H, $PCH(CH_3)_2$), 1.42 and 1.44 (d, 3 H each, $^2J_{HP}$ = 7.2, $^2J_{HP'}$ = 7.6 Hz, PCH_3), 2.39 and 2.52 (m, 2 H each, $PCH(CH_3)_2$). ^{31}P-{^{1}H} NMR (161.89 MHz, $CDCl_3$, 273 K): δ 44.2 and 45.4 (d, $^2J_{PP'}$ = 23.2 Hz). ^{13}C-{^{1}H} NMR (50.31 MHz, 293 K, $CDCl_3$): δ 8.13 and 8.70 (d, $^1J_{CP}$ = 22.2, $^1J_{CP'}$ = 22.7, PCH_3), 18.0, 18.9 and 19.3 (m, $PCH(CH_3)_2$), 27.0, 27.6, 28.0 and 28.5 (d, $^1J_{CP}$ = 15.9, 17.2, 10.6, 10.2, $PCH(CH_3)_2$) and 199.5 (t, $^2J_{CP} = {}^2J_{CP'}$ = 16.7 Hz, CO).

$[RuCl_2(CO)_2(P^iPr_2Me)_2]$ 2. Carbon monoxide was bubbled through a solution of complex **1** (0.11 g, 0.25 mmol) in CH_2Cl_2 (10 ml) for 5 min at room temperature, causing an immediate change to colourless. The mixture was stirred for 30 min under a CO atmosphere, and then the removal of the solvent in vacuum yielded a white solid, which was washed with light petroleum and dried. Yield: 0.12 g (100%). Calc. for $C_{16}H_{34}Cl_2P_2O_2$Ru: C, 39.0; H, 6.91. Found: C, 39.8; H, 6.87%. IR (Nujol, cm^{-1}): ν(CO) 2053, 1971. ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ 1.20–1.32 (m, 24 H, $PCH(CH_3)_2$), 1.52 and 1.54 (d, 3 H each, $^2J_{HP}$ = 4.5, $^2J_{HP'}$ = 4.1 Hz, PCH_3), 2.20, 2.47, 2.65 and 2.67 (m, 1 H each, $PCH(CH_3)_2$). ^{31}P-{^{1}H} NMR (161.89 MHz, $CDCl_3$, 273 K): δ 15.2 and 40.5 (d, $^2J_{PP'}$ = 23.3 Hz). ^{13}C-{^{1}H} NMR (50.31 MHz, 293 K, $CDCl_3$): δ 3.47 and 8.94 (d, $^1J_{PC}$ = 26.3, $^1J_{P'C}$ = 30.2, PCH_3), 17.8–18.7 (m, $PCH(CH_3)_2$), 24.5, 25.2, 28.2, 28.9 (d, $^1J_{CP}$ = 22.4, 23.1, 28.0 and 26.5, $PCH(CH_3)_2$), 188.9 (s, CO) and 195.5 (dd, $^2J_{CP} = {}^2J_{CP'}$ = 12.3 Hz, CO).

$[RuCl_2(CO)(^tBuNC)(P^iPr_2Me)_2]$ 3a and 3b. *Complex 3a*. To a suspension of complex **1** (0.11 g, 0.25 mmol) in THF (10 ml) was added *tert*-butyl isocyanide (55 µl, 0.50 mmol) yielding a colourless solution after 5 min. The solution was stirred for 30 min more, concentrated to *ca.* 2 ml and by addition of light petroleum a white solid precipitated. Yield: 0.13 g (93%). Calc. for $C_{20}H_{43}Cl_2NOP_2Ru$: C, 43.8; H, 7.85. Found: C, 42.8; H, 7.82%. IR (Nujol, cm^{-1}): ν(CO) 1948, ν(CN) 2180. ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ 1.22–1.35 (m, 24 H, $PCH(CH_3)_2$), 1.50 and 1.52 (d, 3 H each, $^2J_{HP}$ = 8.7, $^2J_{HP'}$ = 9.1 Hz, PCH_3), 1.54 (s, 9 H, $CNC(CH_3)_3$), 2.25, 2.50, 2.56 and 2.63 (m, 1 H each, $PCH(CH_3)_2$). ^{31}P-{^{1}H} NMR (161.89 MHz, $CDCl_3$, 273 K): δ 16.4 and 40.8 (d, $^2J_{PP'}$ = 24.0 Hz). ^{13}C-{^{1}H} NMR (50.31 MHz, 293 K, $CDCl_3$): δ 3.0 (t, $^1J_{PC} = {}^1J_{P'C}$ = 25.2, PCH_3), 18.0, 18.2, 18.9 and 19.0 (s, $PCH(CH_3)_2$), 26.1 and 26.7 (t, $^1J_{CP}$ = 22.0, 25.5, $PCH(CH_3)_2$), 30.6 (s, $CNC(CH_3)_3$), 54.4 (s, $CNC(CH_3)_3$), 157.6 (s, $CNC(CH_3)_3$) and 201.0 (t, $^2J_{CP}$ = 15 Hz, CO).

Complex 3b. To a solution of complex **1** (0.11 g, 0.25 mmol) in CH_2Cl_2 (10 ml) was added *tert*-butyl isocyanide (55 µl, 0.50 mmol), resulting in a change to colourless. After stirring for 30 min at room temperature, the solvent was removed under vacuum, yielding a white solid which was washed with diethyl ether and dried. Yield: 0.15 g (96%). Calc. for $C_{20}H_{43}Cl_2NOP_2Ru$: C, 43.8; H, 7.85. Found: C, 43.9; H, 7.88%. IR (Nujol, cm^{-1}): ν(CO) 1969, ν(CN) 2180 and 2206. ^{1}H NMR (400 MHz, 293 K,

$CDCl_3$): δ 1.20–1.32 (m, 12 H, $PCH(CH_3)_2$), 1.47 (d, 3 H, $^2J_{HP}$ = 9.0 Hz, PCH_3), 1.60 (s, 9 H, $CNC(CH_3)_3$), 2.26 and 2.47 (m, 1H each, $PCH(CH_3)_2$). ^{31}P-{^{1}H} NMR (161.89 MHz, $CDCl_3$, 273 K): δ 20.1 (s). ^{13}C-{^{1}H} NMR (50.31 MHz, 293 K, $CDCl_3$): δ 6.07 (m, PCH_3), 18.0, 18.2, 18.6 and 19.0 (s, $PCH(CH_3)_2$), 25.8 and 27.4 (m, $PCH(CH_3)_2$), 30.2 (s, $CNC(CH_3)_3$), 59.6 (s, $CNC(CH_3)_3$), 163.5 (s, $CNC(CH_3)_3$) and 195.0 (t, $^2J_{CP}$ = 13.2 Hz, CO).

[$RuCl_2(CO)(NHCPh_2)(P^iPr_2Me)_2$] 4. A solution of complex **1** (0.11 g, 0.25 mmol) in CH_2Cl_2 was treated with diphenylmethanimine (53 µl, 0.30 mmol) and stirred for 2 h. Solvent evaporation under vacuum left a yellow solid, which was washed with light petroleum. The crude product was recrystallized from a two-layered solution of CH_2Cl_2 and light petroleum (1 : 1). Yield: 0.15 g (94%). Calc. for $C_{28}H_{45}Cl_2NOP_2Ru$: C, 52.0; H, 6.97. Found: C, 52.5; H, 7.09%. IR (Nujol, cm^{-1}): ν(CO) 1936, ν(NH) 3217. ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ 1.12–1.43 (m, 24 H, $PCH(CH_3)_2$), 0.96 and 1.05 (dd, 3 H each, $^2J_{HP}$ = 7.0, $^2J_{HP'}$ = 6.9 Hz, PCH_3), 2.04, 2.18, 2.90 and 2.95 (m, 1 H each, $PCH(CH_3)_2$), 7.38, 7.48 and 7.83 (m, 10 H, $HNC(C_6H_5)_2$) and 10.8 (br s, $HNCPh_2$). ^{31}P-{^{1}H} NMR (161.89 MHz, $CDCl_3$, 273 K): δ 31.9 and 37.0 (d, $^2J_{PP'}$ = 26.8 Hz). ^{13}C-{^{1}H} NMR (50.31 MHz, 293 K, $CDCl_3$): δ 6.14 and 6.67 (d, $^1J_{PC}$ = $^1J_{P'C}$ = 12.9, PCH_3), 18.1, 19.2 and 20.0 (m, $PCH(CH_3)_2$), 25.3, 26.6, 27.1 and 28.5 (d, $^1J_{CP}$ = 28.3, 24.5, 24.7 and 25.6, $PCH(CH_3)_2$), 128.1, 128.7, 129.1, 130.1, 130.3, 131.5, 137.0 and 138.4 (s, $HNC(C_6H_5)_2$), 179.5 (s, $HNC(C_6H_5)_2$) and 200.5 (t, $^2J_{CP}$ = 15.5 Hz, CO).

[$RuCl_2(CO)(L)(P^iPr_2Me)_2$] (L = Hpz 5 or 3,5-$Me_2$Hpz 6). These compounds were prepared in a similar way to the previous imine adduct, with the reagents pyrazole (34 mg, 0.50 mmol) or 3,5-dimethylpyrazole (48 mg, 0.50 mmol) respectively, stirring the mixtures for 4 h and yielding a greenish white and a brown solid respectively.

Complex **5**. Yield 0.09 g (68%). Calc. for $C_{18}H_{38}Cl_2N_2OP_2Ru$: C, 40.6; H, 7.14. Found: C, 40.1; H, 7.29%. IR (Nujol, cm^{-1}): ν(CO) 1928, ν(NH) 3123 and 3331. ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ 0.90–1.42 (m, 30 H, $PCH(CH_3)_2$ and PCH_3), 2.13 and 2.86 (m, 2 H each, $PCH(CH_3)_2$), 6.38, 7.58 and 7.76 (s, 1 H each, $C_3H_3N_2$) and 12.58 (br s, 1 H, NH). ^{31}P-{^{1}H} NMR (161.89 MHz, $CDCl_3$, 273 K): δ 34.2 and 36.2 (d, $^2J_{PP'}$ = 26.7 Hz). ^{13}C-{^{1}H} NMR (50.31 MHz, 293 K, $CDCl_3$): δ 6.12 and 6.92 (d, $^1J_{PC}$ = $^1J_{P'C}$ = 26.7, PCH_3), 17.8–19.8 (m, $PCH(CH_3)_2$), 25.6, 26.7, 27.0 and 28.8 (d, $^1J_{CP}$ = 27.8, 25.1, 25.4 and 25.4, $PCH(CH_3)_2$), 107.2, 129.3 and 141.7 (s, $C_3H_3N_2$) and 200.8 (dd, $^2J_{CP}$=14.8, $^2J_{CP'}$ = 17.1 Hz, CO).

Complex **6**. Yield 0.13 g (93%). Calc. for $C_{20}H_{42}Cl_2N_2OP_2Ru$: C, 42.8; H, 7.49. Found: C, 42.5; H, 7.30%. IR (Nujol, cm^{-1}): ν(CO) 1923, ν(NH) 3209 and 3250. ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ 0.98–1.39 (m, 24 H, $PCH(CH_3)_2$), 1.39 and 1.44 (d, 3 H each, $^2J_{HP}$ = 9.1, $^2J_{HP'}$ = 9.5 Hz, PCH_3), 2.02, 2.36, 2.78 and 2.98 (m, 1 H each, $PCH(CH_3)_2$), 2.23 and 2.53 (s, 3 H each, $(CH_3)_2C_3HN_2$), 5.85 (s, 1 H, $(CH_3)_2C_3HN_2$) and 12.26 (br s, 1 H, NH). ^{31}P-{^{1}H} NMR (161.89 MHz, $CDCl_3$, 273 K): δ 32.5 and 35.7 (d, $^2J_{PP'}$ = 26.4 Hz). ^{13}C-{^{1}H} NMR (50.31 MHz, 293 K, $CDCl_3$): δ 6.20 and 7.34 (d, $^1J_{CP}$ = 27.0, $^1J_{CP'}$ = 26.5, PCH_3), 18.21–19.97 (m, $PCH(CH_3)_2$), 26.0, 26.3, 26.8 and 28.1 (d, $^1J_{CP}$ = 25.3, 23.8, 28.0 and 25.7, $PCH(CH_3)_2$), 11.0 and 15.6 (s, $(CH_3)_2C_3HN_2$), 107.6, 139.9 and 152.2 (s, $(CH_3)_2C_3HN_2$) and 200.2 (t, $^2J_{CP}$ = 15.6 Hz, CO).

[{$RuCl(CO)(P^iPr_2Me)_2$}$_2$(µ-Cl)(µ-SPh)] 7. A solution of complex **1** (0.11 g, 0.25 mmol) in CH_2Cl_2 (10 ml) was treated with benzenethiol (51 µl, 0.50 mmol) with an immediate change from yellow to green. The solution was stirred for 4 h. The solvent was removed *in vacuo* and the residue washed with Et_2O, isolating a green solid. Yield: 0.11 g (88%). Calc. for $C_{36}H_{73}Cl_3O_2P_4Ru_2S$: C, 43.1; H, 7.34%. Found: C, 43.3; H, 7.34%. IR (Nujol, cm^{-1}): ν(CO) 1967 and 1949. ^{1}H NMR (400 MHz, 293 K, CD_3COCD_3): δ 1.0–1.4 (m, 24 H, $PCH(CH_3)_2$), 1.58 and 1.61 (d, 3 H each, $^2J_{HP}$ = 4.8, $^2J_{HP'}$ = 5.5 Hz, PCH_3), 2.47, 2.55 and 2.72 (m, 4 H, $PCH(CH_3)_2$), 7.31 and 8.24 (m, 5 H, C_6H_5S). ^{31}P-{^{1}H} NMR (161.89 MHz, 273 K, CD_3COCD_3): δ 44.7 and 29.2 (d, $^2J_{PP'}$ = 20.5 Hz). ^{13}C-{^{1}H} NMR (50.31 MHz, 293 K, CD_3COCD_3): δ 7.98 and 9.18 (d, $^1J_{CP}$ = 27.5, $^1J_{CP'}$ = 32.0 Hz, PCH_3), 18.23–19.8 (m, $PCH(CH_3)_2$), 27.3, 28.2, 28.5 and 29.8 (d, $^1J_{CP}$ = 27.3, 28.2, 28.5 and 29.8, $PCH(CH_3)_2$), 128.4, 128.9, 129.1 and 134.9 (s, C_6H_5S), 203.1 (t, $^2J_{CP}$ = $^2J_{CP'}$ = 16.6 Hz, CO). Mass spectrum (ESI-MS): *m*/*z* 967 (M − SPh, 100%) and 895 (M − Cl, 100%).

[$RuCl_2(CO)(PySH)(P^iPr_2Me)_2$] 8a and 8b. A solution of complex **1** (0.11 g, 0.25 mmol) in CH_2Cl_2 (10 ml) was treated with an excess of 2-sulfanylpyridine (56 mg, 0.50 mmol) with continuous stirring at room temperature for 30 min, and a gradual change from yellow to red was observed. The solvent was removed in vacuum and the residue washed with Et_2O, isolating a red solid which mostly corresponds to complex **8a**. If the reaction is stirred for more than 4 h, **8b** is the only product. Yield: 0.13 g (90%). Calc. for $C_{20}H_{39}Cl_2NOP_2RuS$: C, 41.7; H, 6.78. Found: C, 41.2; H, 6.84%. Complex **8a**: IR (Nujol, cm^{-1}) ν(NH) 3182, ν(CO) 1931, ν(C=C/C=N) 1606, 1587; ^{1}H NMR (400 MHz, 293 K, $CDCl_3$) δ 1.18–1.32 (m, 24 H, $PCH(CH_3)_2$), 1.42 and 1.44 (d, 3 H each, $^2J_{HP}$ = $^2J_{HP'}$ = 8.2, PCH_3), 2.65 and 2.80 (m, 2 H each, $PCH(CH_3)_2$), 6.78 (t, $^3J_{HH}$ = 6.4, S=CCHC*H*), 7.42 (t, $^3J_{HH}$ = 6.0, NCHC*H*), 7.54 (d, $^3J_{HH}$ = 6.0, S=CC*H*), 7.89 (t, $^3J_{HH}$ = 6.0 Hz, NCH) and 14.39 (br s, NH); ^{31}P-{^{1}H} NMR (161.89 MHz, $CDCl_3$, 273 K) δ 28.7 and 37.2 (d, $^2J_{PP'}$ = 24 Hz); ^{13}C-{^{1}H} NMR could not be obtained because of the quickness of the isomerization process. Complex **8b**: IR (Nujol, cm^{-1}) ν(NH) 3182, ν(CO) 1939, ν(C=C/C=N) 1608, 1580; ^{1}H NMR (400 MHz, 293 K, $CDCl_3$) δ 1.18–1.32 (m, 24 H, $PCH(CH_3)_2$), 1.42 (d, 6 H, J_{HP} = 8.3, PCH_3), 2.68 and 2.80 (m, 2 H each, $PCH(CH_3)_2$), 6.92 (t, $^3J_{HH}$ = 6.4, S=CCHC*H*), 7.39 (t, $^3J_{HH}$ = 6.4, NCHC*H*), 7.63 (d, $^3J_{HH}$ = 8.0, S=CCH), 8.13 (t, $^3J_{HH}$ = 6.0 Hz, NCH) and 14.78 (br s, NH); ^{31}P-{^{1}H} NMR (161.89 MHz, $CDCl_3$, 273 K) δ 27.8 (s); ^{13}C-{^{1}H} NMR (50.31 MHz, 293 K, $CDCl_3$) δ 5.8 (m, PCH_3), 17.6, 18.1 and 18.9 (s, $PCH(CH_3)_2$), 25.9 and 26.3 (m, $PCH(CH_3)_2$), 116.3 (s, SCCHC*H*), 130.8, 137.4, and 138.5 (s, NCHCH and S=CCH), 169.6 (s, S=CN) and 200.3 (t, $^1J_{CP}$=14.1 Hz, CO).

[$RuCl(S_2CNEt_2)(CO)(P^iPr_2Me)_2$] 9. To a solution of complex **1** (0.11 g, 0.25 mmol) in CH_2Cl_2 (10 ml) was added sodium diethyldithiocarbamate (51 mg, 0.30 mmol). The resulting suspension was stirred for 12 h and then filtered through Celite. Removal of the solvent by vacuum afforded a brown microcrystalline solid which was washed with light petroleum. Yield: 0.14 g (97%). Calc. for $C_{20}H_{44}ClNOP_2RuS_2$: C, 41.6; H, 7.62. Found: C, 40.9; H, 7.47%. IR (Nujol, cm^{-1}): ν(CO) 1921, ν(C=N) 1505. ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ 1.17–1.35 (m, 24 H, $PCH(CH_3)_2$), 1.40 (d, 6 H, $^2J_{HP}$ = 8.2 Hz, PCH_3), 2.14 and 2.30 (m, 2 H each, $PCH(CH_3)_2$), 1.24 (t, 6 H, $^3J_{Ha,CH_3}$ = $^3J_{Hb,CH_3}$ = 7, $S_2CN(CH_aH_bCH_3)_2$), 3.65 and 3.81 (m, 2 H each, $^3J_{CH_3,Ha}$ = $^3J_{CH_3,Hb}$ = 7 Hz, $S_2CN(CH_aH_bCH_3)_2$). ^{31}P-{^{1}H} NMR (161.89 MHz, $CDCl_3$, 273 K): δ 30.9 (s). ^{13}C-{^{1}H} NMR (50.31 MHz, 293 K, $CDCl_3$): δ 6.80 (m, PCH_3), 18.3, 18.8 and 19.3 (s, $PCH(CH_3)_2$), 27.4 and 28.2 (m, $PCH(CH_3)_2$), 12.3 (s, $S_2CN(CH_2CH_3)_2$), 43.1 (s, $S_2CN(CH_2CH_3)_2$, 200.9 (t, $^2J_{CP}$ = $^2J_{CP'}$ = 13.8 Hz, CO) and 211.4 (s, $S_2CN(CH_2CH_3)_2$.

[$RuCl(S_2COR)(CO)(P^iPr_2Me)_2$] (R = Me 10, Et 11 or ^{i}Pr 12). An experimental procedure identical to that for **9** was followed for the preparation of these complexes, using the corresponding potassium alkyl dithiocarbonate KS_2COR (0.3 mmol). The compounds were recrystallized from CH_2Cl_2 by slow evaporation of the solvent.

Complex **10**. Yield: 0.13 g (97%). Calc. for $C_{17}H_{37}ClO_2P_2RuS_2$: C, 38.0; H, 6.90. Found: C, 37.8; H, 6.98%. IR (Nujol, cm^{-1}): *ν*(CO) 1928. ^1H NMR (400 MHz, 293 K, $CDCl_3$): δ 1.19–1.33 (m, 24 H, $PCH(CH_3)_2$), 1.43 (d, 6 H, $J_{HP} = 8.5$ Hz, PCH_3), 2.20 and 2.40 (m, 2 H each, $PCH(CH_3)_2$) and 4.14 (s, 3 H, S_2COCH_3). ^{31}P-{^1H} NMR (161.89 MHz, $CDCl_3$, 273 K): δ 32.8 (s). ^{13}C-{^1H} NMR (50.31 MHz, 293 K, $CDCl_3$): δ 7.12 (m, PCH_3), 18.3, 18.8 and 19.3 (s, $PCH(CH_3)_2$), 27.8 and 28.3 (m, $PCH(CH_3)_2$), 57.0 (s, S_2COCH_3), 199.2 (t, $^2J_{CP} = {}^2J_{CP'} = 15.3$ Hz, CO) and 230.9 (s, S_2COCH_3).

Complex **11**. Yield: 0.13 g (94%). Calc. for $C_{18}H_{39}ClO_2P_2RuS_2$: C, 39.3; H, 7.09. Found: C, 39.3; H, 7.19%. IR (Nujol, cm^{-1}): *ν*(CO) 1925. ^1H NMR (400 MHz, 293 K, $CDCl_3$): δ 1.17–1.34 (m, 24 H, $PCH(CH_3)_2$), 1.42 (d, 6 H, $J_{HP} = 8.4$, PCH_3), 2.16 and 2.38 (m, 2 H each, $PCH(CH_3)_2$), 1.41 (t, 3 H, $J_{CH_3,CH_2} = 7.2$, $S_2COCH_2CH_3$) and 4.59 (c, 2 H, $J_{CH_2,CH_3} = 7.2$ Hz, $S_2COCH_2CH_3$). ^{31}P-{^1H} NMR (161.89 MHz, $CDCl_3$, 273 K): δ 32.7 (s). ^{13}C-{^1H} NMR (50.31 MHz, 293 K, $CDCl_3$): δ 7.12 (m, PCH_3), 18.3, 18.8 and 19.3 (s, $PCH(CH_3)_2$), 27.8 and 28.2 (m, $PCH(CH_3)_2$), 13.8 (s, $S_2COCH_2CH_3$), 66.9 (s, $S_2COCH_2CH_3$), 199.3 (t, $^2J_{CP} = {}^2J_{CP'} = 15$ Hz, CO) and 230.2 (s, $S_2COCH_2CH_3$).

Complex **12**. Yield: 0.14 g (100%). Calc. for $C_{19}H_{41}ClO_2P_2RuS_2$: C, 40.4; H, 7.27. Found: C, 41.1; H, 7.26%. IR (Nujol, cm^{-1}): *ν*(CO) 1936. ^1H NMR (400 MHz, 293 K, $CDCl_3$): δ 1.17–1.34 (m, 24 H, $PCH(CH_3)_2$), 1.42 (d, 6 H, $^2J_{HP} = 8.4$, PCH_3), 1.40 (d, 6 H, $^3J_{CH_3,CH} = 6.4$, $S_2COCH(CH_3)_2$), 2.16 and 2.38 (m, 2 H each, $PCH(CH_3)_2$) and 5.57 (sept, $^3J_{CH,CH_3} = 6.4$ Hz, $S_2COCH(CH_3)_2$). ^{31}P-{^1H} NMR (161.89 MHz, $CDCl_3$, 273 K): δ 32.5 (s). ^{13}C-{^1H} NMR (50.31 MHz, 293 K, $CDCl_3$): δ 7.1 (m, PCH_3), 18.3, 18.8 and 19.3 (s, $PCH(CH_3)_2$), 27.9 and 28.2 (m, $PCH(CH_3)_2$), 21.8 (s, $S_2COCH(CH_3)_2$), 75.6 (s, $S_2COCH(CH_3)_2$), 199.5 (t, $^2J_{CP} = 14$ Hz, CO) and 229.7 (s, $S_2COCH(CH_3)_2$).

[RuCl(acac)(CO)(P^{i}Pr$_2$Me)$_2$] 13. To a solution of complex **1** (0.11 g, 0.25 mmol) in CH_2Cl_2 (5 ml) was added a suspension formed by addition of potassium *tert*-butoxide (50 mg, 0.25 mmol) to 5 ml CH_2Cl_2–acetylacetone (1:1). The resulting suspension was stirred for 12 h at room temperature and then filtered through Celite. Removal of the solvent by vacuum yielded a brown oil which was washed with Et_2O. The oil solidified at temperatures below −20 °C. Yield: 0.08 g (65%). Calc. for $C_{20}H_{41}ClO_3P_2Ru$: C, 45.5; H, 7.77. Found: C, 45.1; H, 7.80%. IR (Nujol, cm^{-1}): *ν*(CO) 1940, *ν*(CO_{acac}) 1590 and 1520. ^1H NMR (400 MHz, 293 K, $CDCl_3$): δ 1.04–1.31 (m, 30 H, $PCH(CH_3)_2$ and PCH_3), 2.15, 2.20, 2.61 and 2.68 (m, 2 H each, $PCH(CH_3)_2$), 1.90 and 1.95 (s, 3 H each, $CH_3COCHCOCH_3$) and 5.36 (s, 1 H, $CH_3COCHCOCH_3$). ^{31}P-{^1H} NMR (161.89 MHz, $CDCl_3$, 273 K): δ 38.5 and 42.9 (d, $^2J_{PP'} = 26.3$ Hz). ^{13}C-{^1H} NMR (50.31 MHz, 293 K, $CDCl_3$): δ 6.26 and 6.68 (d, $^1J_{CP} = 26.6$, $^1J_{CP'} = 25.8$, PCH_3), 17.4–19.0 (m, $PCH(CH_3)_2$), 24.6, 25.8, 26.1 and 26.3 (d, $PCH(CH_3)_2$), 25.5 and 28.0 (s, $CH_3COCHCOCH_3$), 100.2 (s, $CH_3COCHCOCH_3$), 185.8 and 188.0 (s, $CH_3COCHCOCH_3$) and 204.2 (t, $^2J_{CP} = {}^2J_{CP'} = 17.2$ Hz, CO).

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