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[Ru(PPh$_3$)$_3$Cl$_2$]-Mediated Transformation of –CH$_3$ into =CHPHPh$_3$ in Biacetylmonoxime Acetyl-/Aroylhydrazones: Ruthenium(III) Complexes with the Transformed Ligands

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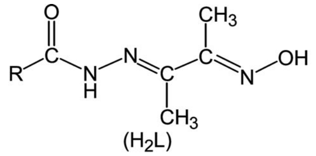
Keywords: Ruthenium / Ligand transformation / Redox properties

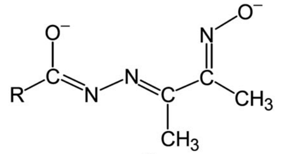
Ruthenium(III) complexes of general formula *trans*-[Ru(^{t}L)(PPh$_3$)Cl$_2$] have been isolated in 58–73 % yields from reactions between [Ru(PPh$_3$)$_3$Cl$_2$] and tridentate Schiff bases (H$_2$L) derived from biacetylmonoxime and acid hydrazides in methanol. The X-ray structures of the complexes reveal unprecedented conversions of methyl groups in the biacetyl fragments of the Schiff bases into triphenyl-vinyl-λ^5-phosphane (=CHPHPh$_3$) moieties in the transformed ligands (^{t}L$^-$). The metal centre in each complex is in a distorted octahedral N$_2$OPCl$_2$ coordination sphere made up of the meridionally spanning N,N,O-donor ^{t}L$^-$, PPh$_3$ and two mutually *trans*-oriented chlorides. In their electronic spectra, the complexes each display four absorptions due to ligand-to-metal and ligand-centred transitions in the 463–260 nm range. All the complexes are one-electron paramagnetic ($\mu_{\text{eff.}}$ at 298 K = 1.81–2.06 μ_B) and display rhombic EPR spectra in frozen (120 K) dichloromethane/toluene (1:1) solutions. Cyclic voltammograms of the complexes in dimethylformamide solutions show substituent-sensitive, quasi-reversible Ru^{IV}/Ru^{III} and Ru^{III}/Ru^{II} couples in the potential ranges of 0.46 to 0.54 V and –0.53 to –0.42 V (vs. Ag/AgCl), respectively.

Introduction

Interest in the coordination complexes of ruthenium is due to their versatile electron- and energy-transfer properties.[1,2] As a result of these properties, ruthenium complexes exhibit a wide range of reactivities and have found applications in various research areas such as artificial photosynthesis, photomolecular devices, probes for biological macromolecules, oxidation catalysts and organic synthesis.[2] We have been working for some time on the chemistry of ruthenium with Schiff bases derived from acid hydrazides.[3] These Schiff bases contain amide functionalities, which can coordinate to the metal ion through their O atoms and promote high oxidation states.[4] Such ligands offer the potential to scrutinize the effect of the metal-bound amide protonation state on the reactivities, structures and physical properties of their complexes.[3,5] The tridentate Schiff base system (H$_2$L; the 2 H represent the dissociable amide and oxime protons) derived from biacetylmonoxime and acid hydrazide contains (in addition to the O-coordinating amide) a second high oxidation state promoting oxime functionality, the protonation state of which is also adjustable.[6] In its deprotonated state (L^{2-}), this Schiff base system would be expected to coordinate to the metal ion through the deprotonated amide-O, the imine-N and the oximate-N atoms, forming two five-membered chelate rings. The oximate fragment is also well known to act as a bridge between two metal centres.[7] In our effort to explore the chemistry of ruthenium with H$_2$L, using [Ru(PPh$_3$)$_3$Cl$_2$] as the starting material, we have found an unprecedented chemical conversion of the –CH$_3$ group at the oxime end of H$_2$L into =CHPHPh$_3$ and have isolated a series of ruthenium(III) complexes **1**–**5** of the transformed ligands (^{t}L$^-$)



(H$_2$L)



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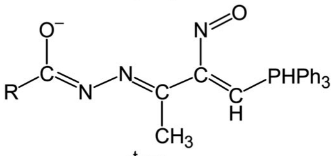

(^{t}L$^-$)

[Ru(^{t}L)(PPh$_3$)Cl$_2$] (**1**–**5**)

R = CH$_3$ (**1**), C$_6$H$_5$ (**2**), 4-CH$_3$-C$_6$H$_4$ (**3**), 4-OCH$_3$-C$_6$H$_4$ (**4**), 4-Cl-C$_6$H$_4$ (**5**)

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with the general formula *trans*-[Ru(^{t}L)(PPh$_3$)Cl$_2$]. In this article we report the syntheses, X-ray structures and physical properties of these complexes.

Results and Discussion

Synthesis and Characterization

Reactions between equimolar amounts of H$_2$L and [Ru(PPh$_3$)$_3$Cl$_2$] in methanol under aerobic conditions produced a series of ruthenium(III) complexes **1**–**5**. All the complexes are brown. In acetonitrile solution, they are electrically non-conducting. The elemental analysis data (Table 1) are consistent with the molecular formulas of the complexes containing the transformed ligands. The effective magnetic moments of these species at room temperature (298 K) are in the 1.81–2.06 μ_B range (Table 1). These values indicate the +3 oxidation state and the low-spin nature of the ruthenium centre in each complex. The complexes were not formed if the reactions between H$_2$L and [Ru(PPh$_3$)$_3$Cl$_2$] were performed under nitrogen, so the oxygen in air is responsible for the oxidation of the metal centre during synthesis.

Spectroscopic Characteristics

None of the infrared spectra of the complexes displays any band corresponding to C=O, N–H or O–H, so the amide and the oxime functionalities of the ligands in **1**–**5** are in deprotonated states. The sharp but weak bands observed at 2851–3056 cm^{-1} are attributable to C–H stretches. A very weak band observed in the 2123–2185 cm^{-1} range is possibly due to the P–H stretch. The C=N stretch appears as a medium to strong band in the 1576–1608 cm^{-1} range.[3,5] The strong band observed in the 1272–1281 cm^{-1} range is perhaps associated with the nitroso fragment of the transformed ligand.[7a,b] Three strong bands at 745–519 cm^{-1} indicate the presence of PPh$_3$ in all the complexes.[3c–f]

The electronic spectra of the complexes in dichloromethane were measured; the data are summarized in Table 1. The spectral profiles of **1**–**5** are very similar and each display four intense absorptions in the 463–260 nm range. The low-energy absorptions are most probably due to ligand-to-metal charge transfer transitions, whereas the highest-energy absorption possibly only involves ligand-centred orbitals.

Although the complexes are paramagnetic, the ^{31}P NMR spectra of **1**–**5** in CDCl$_3$ were recorded to confirm the presence of two different types of P atoms. Indeed, each spectrum displays two signals at $\delta \approx 23$ and ca. 21 ppm.

The X-band EPR spectra of **1**–**5** in frozen (120 K) dichloromethane/toluene (1:1) solution are very similar and each display three distinct signals (Table 2). A representative spectrum is shown in Figure 1. Such an EPR spectrum is characteristic of a distorted octahedral ruthenium(III) species with $S = 1/2$ ground spin state.[3b,d–f,8]

Table 2. EPR[a] and cyclic voltammetric data.[b]

Complex	g_1	g_2	g_3	$E_{1/2}$ [V] (ΔE_p [mV])[c]
1	2.20	2.04	1.99	–0.42 (150)
2	2.19	2.03	1.98	–0.47 (100), 0.53 (100)
3	2.20	2.04	1.98	–0.49 (160), 0.52 (100)
4	2.20	2.04	1.98	–0.54 (110), 0.46 (80)
5	2.20	2.04	1.99	–0.45 (110), 0.55 (90)

[a] In 1:1 dichloromethane/toluene at 120 K. [b] In dimethylformamide solution (298 K) at a scan rate of 50 mV s^{-1}. [c] $E_{1/2} = (E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; $\Delta E_p = E_{pa} - E_{pc}$.

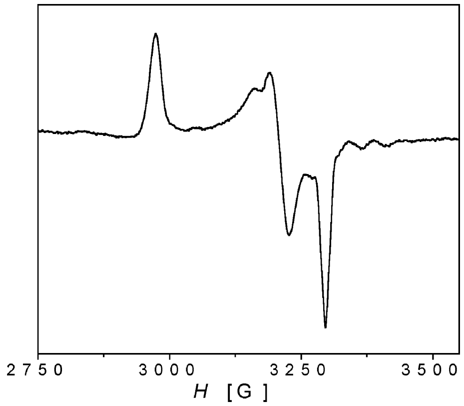


Figure 1. EPR spectrum of [Ru(^{t}L)(PPh$_3$)Cl$_2$] (R = 4-CH$_3$O-C$_6$H$_4$, **4**) in frozen (120 K) dichloromethane/toluene (1:1) solution.

Electrochemical Properties

The electron-transfer properties of **1**–**5** in dimethylformamide solution were investigated by cyclic voltammetry; the potential data are given in Table 2. Each complex displays a reduction response with the $E_{1/2}$ value in the potential range of –0.53 to –0.42 V. Except for **1**, the complexes (**2**–**5**) also show oxidation responses, the $E_{1/2}$ values of which are at 0.46 to 0.55 V. Two representative cyclic voltammog-

Table 1. Elemental analysis,[a] electronic spectroscopic[b] and magnetic susceptibility[c] data.

Complex	% C	% H	% N	λ_{max} [nm] ($10^{-3} \times \varepsilon$ [M^{-1} cm^{-1}])	μ_{eff} [μ_B]
1	59.04 (59.30)	4.31 (4.50)	4.57 (4.94)	453 (18.2), 337 (22.2), 278[d] (18.9), 268[d] (21.8)	2.06
2	61.62 (61.85)	4.28 (4.42)	4.34 (4.60)	457 (6.1), 362 (11.8), 334[d] (10.8), 265[d] (21.9)	1.81
3	62.06 (62.21)	4.29 (4.57)	4.42 (4.53)	453 (4.8), 371 (11.2), 325 (12.9), 260[d] (28.3)	1.89
4	60.87 (61.15)	4.21 (4.49)	4.25 (4.46)	457 (10.1), 372 (20.6), 294[d] (19.2), 270[d] (26.3)	1.99
5	59.48 (59.60)	4.02 (4.15)	4.29 (4.44)	463 (12.6), 371 (21.6), 335[d] (17.3), 268 (29.6)	1.82

[a] Calculated values are in parentheses. [b] In dichloromethane solution. [c] At 298 K. [d] Shoulder.

rams are shown in Figure 2. The peak currents of both reduction and oxidation responses are comparable with known one-electron redox processes under identical conditions.[3,7,9] Both the protonated and the deprotonated (in the presence of NaOH) Schiff bases are electrochemically inactive in the potential ranges described above. As the coordinated ligands each contain the high oxidation state stabilizing amide functionality, the oxidation response is assigned to the ruthenium(IV)/ruthenium(III) couple. The reduction response is assigned to the ruthenium(III)/ruthenium(II) couple. The trends both in the reduction potentials and in the oxidation potentials observed for **2**–**5** reflect the effects of the electronic natures of the substituents (R) on the aroyl fragments of the transformed ligands ($^{t}L^{-}$). For the most strongly electron-releasing substituent (R = OCH_3) both reduction and oxidation of the metal centre occur at the lowest potentials, while for the most strongly electron-withdrawing substituent (R = Cl) they occur at the highest potentials. Satisfactory linear relationships are observed both for reduction and for oxidation when the corresponding $E_{1/2}$ values are plotted against the Hammett substituent constants (σ_p).[10] The $\Delta E_{1/2}$ value is constant (1 V) for all four complexes, and as a result two essentially parallel straight lines are obtained in the Hammett plot (Figure 3).

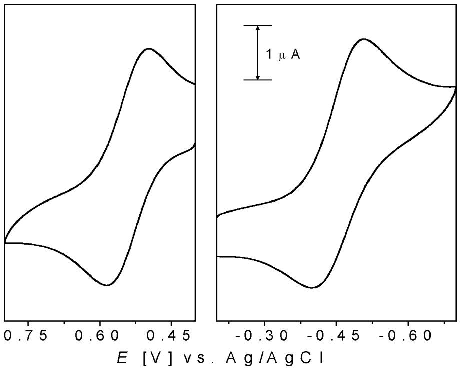


Figure 2. Cyclic voltammograms (scan rate 50 mV s^{-1}) of $[Ru(^{t}L)(PPh_3)Cl_2]$ (R = 4-Cl-C_6H_4, **5**) in dimethylformamide (0.1 M TBAP) at a platinum electrode (298 K).

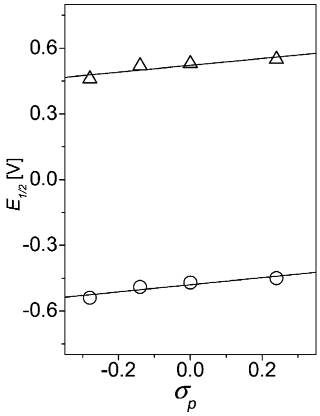


Figure 3. Correlations between the $E_{1/2}$ values for the $Ru^{III} \rightarrow Ru^{IV}$ oxidation (Δ) and the $Ru^{III} \rightarrow Ru^{II}$ reduction (O) with the Hammett substituent constants. The straight lines represent linear least-squares fits.

Description of Molecular Structures

The molecular structures of all five complexes are very similar, each revealing a phosphane attached to the carbon atom of the methyl group at the oxime end of the original Schiff base system. The structures of **3** and **5** are depicted in Figure 4 and the structures of the remaining three complexes **1**, **2** and **4** are provided in the Supporting Information (Figures S1–S3). Selected bond lengths and angles are summarized in Table 3. In each complex, the metal centre is in a distorted octahedral N_2OPCl_2 coordination sphere. The meridionally spanning N,N,O-donor transformed ligand ($^{t}L^{-}$) and the phosphane form an N_2OP square-plane around the metal ion. The remaining two axial sites are occupied by the two chlorine atoms. The two *trans*-Ru–Cl bond lengths are very similar and within the range reported for complexes containing the *trans*-$\{RuCl_2\}^+$ unit.[11] The equatorial Ru–P2 bond length is unexceptional.[3d,12] Interestingly, the Ru–N1(oxime) bond

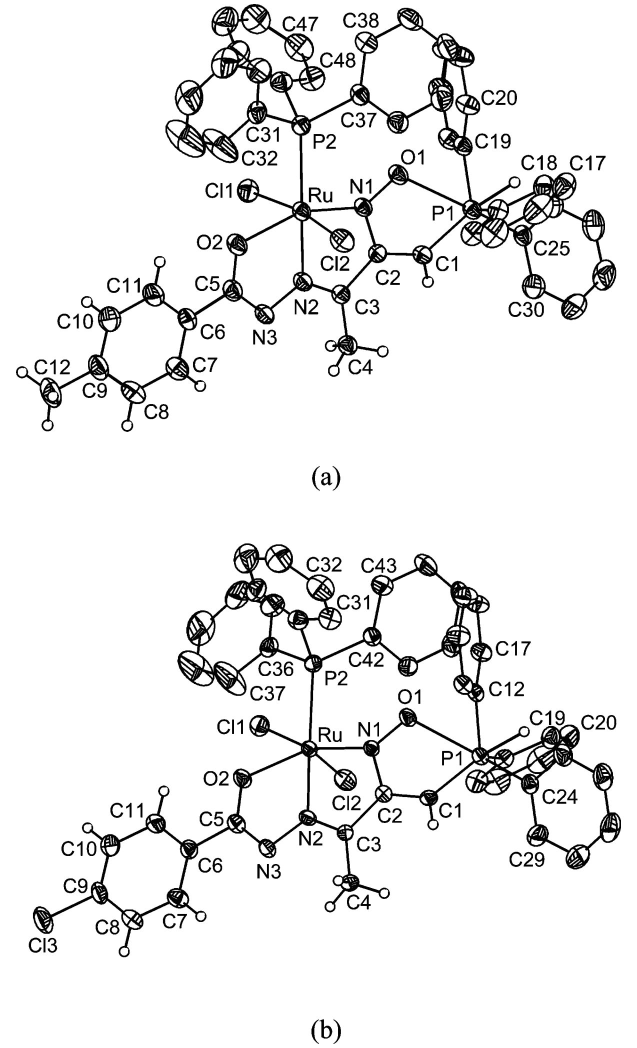


Figure 4. Molecular structures of *trans*-$[Ru(^{t}L)(PPh_3)Cl_2]$: a) **3** (R = 4-CH_3-C_6H_4) and b) **5** (R = 4-Cl-C_6H_4). All non-hydrogen atoms are represented by their 30% probability thermal ellipsoids. For clarity, H atoms of the phenyl rings connected to the P atoms are omitted and selected C atoms of these phenyl rings are labeled.

lengths in these complexes, in which each oximate exists as a neutral nitroso group (vide infra), are smaller than those in ruthenium(III) complexes with N-coordinating normal oximates.[11a,13] Perhaps better π-backbonding in the Ru–N(nitroso) bond than in the Ru–N(imine) bond causes this difference. The Ru–O2(deprotonated amide) and the Ru–N2(imine) bond lengths are comparable with the bond lengths observed in ruthenium(III) complexes and shorter than those reported for ruthenium(II) complexes containing the same coordinating atoms.[3] Interestingly, the oxime O atom is very close to the P atom of the transformed ligand (Figure 4). The P1–O1 distances are in the 2.474(2)–2.600(3) Å range. These distances suggest fairly strong coordination of the O atoms to the P atoms.[14] As a result of this O-coordination, each P atom is in a distorted trigonal bipyramidal C_4O geometry in which the O atom and one of the phenyl ring C atoms occupy the axial sites [O–P–C, 172.0(1)–176.9(3)°] (Figure 5). Each P atom is displaced by 0.419(2) to 0.446(3) Å towards the axial phenyl C atom. The C5–O2, C5–N3 and N2–N3 bond lengths (Figure 4, Table 3) are in the 1.27(1)–1.289(4), 1.326(6)–1.35(1) and 1.349(8)–1.375(5) Å ranges, respectively. These values clearly indicate that the amide functionality of the tridentate ligand is in the enolate form.[3,5] If the oxime end of the tridentate ligand was in the normal oximate form,[7] the transformed ligand would be dianionic, and in view of the neutral characters of these complexes, zwitterionic structures (**I**) are the only possibility for **1**–**5**. However, the O1–N1 [1.255(3)–1.271(4) Å], N1–C2 [1.451(5)–1.464(4) Å] and C2–C1 [1.33(1)–1.353(6) Å] bond lengths (Figure 4, Table 3) at the oxime ends of the tridentate ligands are very different from the corresponding bond lengths in complexes of oximates.[7,11a,13] The significantly longer N1–C2 bonds

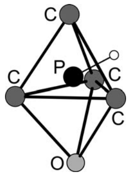
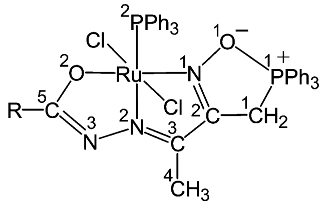


Figure 5. Face-capped trigonal-bipyramidal PHC_4O.



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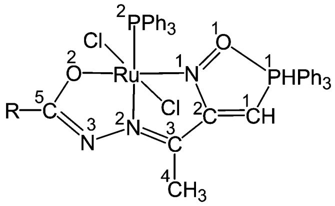

II

Table 3. Selected bond lengths [Å] and angles [°] for **1**·0.5 $C_6H_5CH_3$, **2**·$C_6H_5CH_3$·0.5 CH_3CN, **3**, **4**·CH_3CN and **5**.

Complex	**1**·0.5 $C_6H_5CH_3$	**2**·$C_6H_5CH_3$·0.5 CH_3CN	**3**	**4**·CH_3CN	**5**
Ru–N(1)	1.876(6)	1.893(3)	1.857(3)	1.880(3)	1.860(3)
Ru–N(2)	1.967(6)	1.984(3)	1.988(3)	1.982(3)	1.973(3)
Ru–O(2)	2.099(5)	2.098(2)	2.090(2)	2.092(2)	2.099(3)
Ru–P(2)	2.367(2)	2.350(1)	2.3856(9)	2.3833(9)	2.387(1)
Ru–Cl(1)	2.363(2)	2.3684(9)	2.363(1)	2.366(1)	2.360(1)
Ru–Cl(2)	2.374(2)	2.3591(9)	2.383(1)	2.377(1)	2.384(1)
P(1)–O(1)	2.517(6)	2.600(3)	2.474(2)	2.511(3)	2.478(3)
O(1)–N(1)	1.269(7)	1.262(3)	1.270(3)	1.255(3)	1.271(4)
N(1)–C(2)	1.452(9)	1.463(4)	1.464(4)	1.461(4)	1.451(5)
C(2)–C(1)	1.33(1)	1.342(5)	1.353(4)	1.341(5)	1.353(6)
O(2)–C(5)	1.27(1)	1.286(4)	1.279(4)	1.289(4)	1.285(6)
C(5)–N(3)	1.35(1)	1.339(4)	1.333(4)	1.336(4)	1.326(6)
N(3)–N(2)	1.349(8)	1.363(4)	1.362(4)	1.359(4)	1.375(5)
N(2)–C(3)	1.293(9)	1.305(4)	1.304(4)	1.300(4)	1.312(5)
N(1)–Ru–N(2)	82.2(3)	83.1(1)	82.5(1)	82.6(1)	82.3(2)
N(1)–Ru–O(2)	159.3(2)	159.3(1)	158.3(1)	159.2(1)	158.1(1)
N(1)–Ru–P(2)	100.8(2)	99.36(9)	95.45(8)	97.65(9)	95.0(1)
N(1)–Ru–Cl(1)	98.6(2)	98.55(8)	98.97(9)	92.81(9)	98.9(1)
N(1)–Ru–Cl(2)	90.2(2)	90.06(8)	90.42(9)	93.14(9)	90.8(1)
N(2)–Ru–O(2)	77.3(2)	76.5(1)	76.5(1)	76.6(1)	76.4(1)
N(2)–Ru–P(2)	176.8(2)	177.57(8)	176.69(8)	179.48(9)	176.1(1)
N(2)–Ru–Cl(1)	87.4(2)	89.04(8)	87.00(9)	85.73(9)	86.9(1)
N(2)–Ru–Cl(2)	89.6(2)	87.39(8)	89.49(9)	88.96(9)	89.6(1)
O(2)–Ru–P(2)	99.7(2)	101.05(7)	105.81(7)	103.12(7)	106.50(9)
O(2)–Ru–Cl(1)	83.7(2)	84.40(7)	85.16(8)	86.88(8)	84.8(1)
O(2)–Ru–Cl(2)	86.5(2)	85.90(7)	84.34(8)	85.38(7)	84.3(1)
P(2)–Ru–Cl(1)	91.20(9)	90.75(4)	90.80(3)	93.82(3)	90.73(4)
P(2)–Ru–Cl(2)	91.33(8)	92.43(3)	93.09(4)	91.45(3)	93.28(5)
Cl(1)–Ru–Cl(2)	170.14(9)	170.22(3)	169.45(4)	171.46(4)	169.11(5)

relative to the authentic imine bond [N2–C3, 1.293(9)–1.312(5) Å] and the short C2–C1 bonds clearly suggest that the former are single bonds and the latter are double bonds in the transformed ligands. Complexes **1**–**5** thus have the structure **II**, which is a tautomer of structure **I**. Structure **II** shows that the P atom (P1) is hexacoordinate and pentavalent, due to the shifting of the H atom from the methylene group of structure **I**. The pentavalent character of this P atom is reflected in the P–C bond lengths.

The P1–C(phenyl) bond lengths are in the 1.798(3)–1.817(3) Å range. These values are significantly shorter than the P2–C(phenyl) bond lengths [1.805(8)–1.844(4) Å] in metal-coordinated PPh_3 in which the P atom (P2) is trivalent. The P–CH= bond lengths are in the 1.772(3)–1.786(8) Å range. In the X-ray structure of each complex we have tried to locate the H atom attached to the pentavalent P atom. However, we were able to locate the H atom only in the cases of **3** and **5**. Interestingly, in each case the H atom was found approximately at the centre of the trigonal face formed by the three phenyl C atoms in the PC_4O distorted trigonal bipyramid (see Figures 4 and 5). Thus, together with this hydrogen, the P atom is hexacoordinate. This hydrogen atom is not involved in any H-bond interaction. The position observed for the H atom – rather than between the O and the P atoms – is not very surprising when one considers the short P–O distance (vide supra), which would make a P–H···O type of interaction very unlikely. Because free refinement of this H atom was unsuccessful in the cases of both **3** and **5**, we have refined it with geometric restraints so that the PHC_4O polyhedron has a face-capped trigonal bipyramidal geometry (Figure 5).

A Plausible Mechanism

The mechanism of the observed transformation of the ligands H_2L in their reactions with $[Ru(PPh_3)_3Cl_2]$ is not very clear at present. However, a plausible mechanism based on the literature is illustrated in Scheme S1 (Supporting Information). In the first step, the ligand binds the metal centre through the deprotonated amide-O, the imine-N and the deprotonated methyl-C in a meridional fashion and the metal centre is oxidized by two electrons. Activation of ligand methyl groups by 16-electron starting materials such as $[Ru(PPh_3)_3Cl_2]$ has been reported before;[15] tetravalent ruthenium in a similar coordination sphere is not uncommon.[3e] Deprotonation of the oxime functionality, formation and reductive detachment of the alkene moiety, coordination of the nitroso group and oxidation of the metal centre by one electron are shown in the second step. In the last two steps, nucleophilic attack to the polarized alkene fragment by PPh_3 and the rearrangement to the final product are shown. Such reactions of alkenes with tertiary phosphanes are known in the literature.[16]

Conclusions

In conclusion, we have demonstrated an unprecedented and facile $[Ru(PPh_3)_3Cl_2]$-mediated chemical transformation of a tridentate Schiff base system derived from biacetylmonoxime and various acid hydrazides. The physical properties and the molecular structures of the resulting ruthenium(III) complexes confirm the transformation in all the ligands used. The observed transformation is most probably triggered by metal-assisted alkyl C–H activation, and the activated methyl group at the oxime end of each ligand system is finally changed to $=CHPHPh_3$. Currently we are studying the reactions of various phosphane-containing, electron-deficient metal ion starting materials with the present Schiff base system and analogous tridentate Schiff bases derived from biacetylmonoxime to explore whether the same or similar chemical transformations can be achieved.

Experimental Section

Materials: The Schiff bases (H_2L) were prepared by a slightly modified procedure reported previously.[17] Treatment of biacetylmonoxime (1 mol-equiv.) with the corresponding acid hydrazide (1 mol-equiv.) in boiling methanol, followed by recrystallization from a methanol/*n*-hexane (1:1) mixture, provided H_2L in 70–90% yields. $[Ru(PPh_3)_3Cl_2]$ was prepared by the procedure reported previously.[18] All other chemicals and solvents were available commercially in analytical grade and were used without further purification.

Physical Measurements: The elemental (C,H,N) analyses were performed with a Thermo Finnigan Flash EA1112 series elemental analyzer. Infrared spectra were recorded as KBr pellets on a Nicolet 5700 FT-IR spectrophotometer. A Cary 100 Bio UV/Vis spectrophotometer was used to record the electronic spectra. The ^{31}P NMR spectra were recorded with a Bruker 400 MHz NMR spectrometer. A Jeol JES-FA200 spectrometer was used to record the X-band EPR spectra of the complexes in frozen (120 K) dichloromethane/toluene (1:1) solutions. Room temperature (298 K) magnetic susceptibilities were measured with a Sherwood Scientific balance. Diamagnetic corrections calculated from Pascal's constants[19] were used to obtain the molar paramagnetic susceptibilities. A Digisun DI-909 conductivity meter was used to measure the solution electrical conductivities. A CH-Instruments model 620A electrochemical analyzer was used for the cyclic voltammetric experiments with dimethylformamide solutions of the complexes containing tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The three electrode measurements were carried out at 298 K under dinitrogen with a platinum disk working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. The potentials reported in this work are uncorrected for junction contributions.

Synthesis of the Complexes: All the complexes **1**–**5** reported in this work were synthesized in 58–69% yields from $[Ru(PPh_3)_3Cl_2]$ and the corresponding biacetylmonoxime aroylhydrazone (1:1 mole ratio) by very similar procedures. Details are therefore given for a representative case.

***trans*-[Ru(^{1}L)(PPh$_3$)Cl$_2$] (R = CH$_3$, 1):** Solid $[Ru(PPh_3)_3Cl_2]$ (307 mg, 0.32 mmol) was added to a methanol solution (30 mL) of biacetylmonoxime acetylhydrazone (50 mg, 0.32 mmol), and the mixture was heated to reflux for 2 h. The resulting brown solution was evaporated to dryness in air. The solid obtained was dissolved in the minimum possible amount of CH_2Cl_2 and transferred to a neutral aluminium oxide column packed with CH_2Cl_2. The first

Table 4. Crystallographic data for **1**·0.5 $C_6H_5CH_3$, **2**·$C_6H_5CH_3$·0.5 CH_3CN, **3**, **4**·CH_3CN and **5**.

Complex	**1**·0.5 $C_6H_5CH_3$	**2**·$C_6H_5CH_3$·0.5 CH_3CN	**3**	**4**·CH_3CN	**5**
Formula	$C_{45.5}H_{42}Cl_2N_3O_2P_2Ru$	$C_{55}H_{49.5}Cl_2N_{3.5}O_2P_2Ru$	$C_{48}H_{42}Cl_2N_3O_2P_2Ru$	$C_{50}H_{45}Cl_2N_4O_3P_2Ru$	$C_{47}H_{39}Cl_3N_3O_2P_2Ru$
M_r [g mol^{-1}]	896.73	1025.39	926.76	983.81	947.17
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	10.495(2)	11.1928(7)	11.4627(6)	10.1099(5)	11.453(2)
b [Å]	14.226(3)	12.3365(8)	13.4604(7)	15.8783(8)	13.501(2)
c [Å]	15.956(4)	18.831(1)	16.0082(9)	16.8109(9)	15.934(2)
α [°]	96.906(4)	104.004(1)	90.744(1)	63.429(1)	90.831(2)
β [°]	106.444(4)	103.723(1)	109.726(1)	85.083(1)	109.503(2)
γ [°]	98.930(4)	94.511(1)	111.061(1)	76.171(1)	111.588(2)
V [Å^3]	2222.9(8)	2425.3(3)	2144.2(2)	2342.9(2)	2132.9(5)
Z	2	2	2	2	2
$D_{\text{calcd.}}$ [g cm^{-3}]	1.340	1.404	1.435	1.395	1.475
μ [mm^{-1}]	0.584	0.545	0.608	0.563	0.674
Measured refl.	20928	28015	24932	24565	21193
Unique refl.	7766	11183	9917	9175	8116
R(int)	0.0937	0.0553	0.0379	0.0441	0.0351
Reflections $I \geq 2\sigma_I$	4506	7757	7171	7194	7083
Parameters refined	499	592	528	557	527
GOF on F^2	0.994	1.031	1.025	1.044	1.087
$R1$, $wR2$ ($I \geq 2\sigma_I$)	0.0817, 0.1852	0.0537, 0.1231	0.0564, 0.1199	0.0525, 0.1093	0.0605, 0.1453
$R1$, $wR2$ (all data)	0.1419, 0.2141	0.0875, 0.1358	0.0837, 0.1318	0.0715, 0.1172	0.0702, 0.1507
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ [e Å^{-3}]	1.373, –0.836	0.863, –0.741	0.734, –0.722	0.783, –0.319	1.339, –0.734

moving, light yellow band eluted with pure dichloromethane was discarded. The following brown band containing **1** was collected with dichloromethane/acetone (10:1) mixture as the eluent. The brown solution thus obtained was evaporated to dryness, and the complex was obtained as a dark solid. The yield was 200 mg (73%).

X-ray Crystallography: Single crystals of **1**–**5** were grown by slow evaporation of the corresponding solutions in dichloromethane/toluene/acetonitrile (1:1:0.5) mixtures. For each crystal, unit cell parameters and the intensity data were obtained with a Bruker-Nonius SMART APEX CCD single-crystal diffractometer, fitted with a graphite monochromator and a Mo-K_α fine-focus sealed tube (λ = 0.71073 Å) operated at 2.0 kW. The detector was placed at a distance of 6.0 cm from the crystal. Data were collected at 298 K in the cases of **1** and **3**–**5** and at 133 K in that of **2**, with a scan width of 0.3° in ω and an exposure time of 10 sec/frame. SMART software was used for data acquisition, and SAINT-Plus software for data extraction.[20] The absorption corrections were performed with the aid of the SADABS program.[21] Complexes **3** and **5** crystallize without any solvent molecule, while the other three complexes crystallize as **1**·0.5 $C_6H_5CH_3$, **2**·$C_6H_5CH_3$·0.5 CH_3CN and **4**·CH_3CN. The space group is $P\bar{1}$ in each case. The structures were solved by direct methods and refined on F^2 by full-matrix, least-squares procedures. In all the structures, the non-hydrogen atoms with unit occupancy were refined with the use of anisotropic thermal parameters. The toluene moiety in **1**·0.5 $C_6H_5CH_3$ was refined with geometric restraints. The non-hydrogen atoms of the solvent molecules with half occupancy both in **1**·0.5 $C_6H_5CH_3$ and in **2**·$C_6H_5CH_3$·0.5 CH_3CN were refined isotropically. The H atoms attached to the P atoms in the =$CHPHPh_3$ fragments could be located in difference Fourier maps only in the cases of **3** and **5**. In each case, this hydrogen atom was refined with geometric restraints and U_{iso}(H) = 1.2 U_{eq}(P). All other hydrogen atoms in **3**, **5** and the remaining three structures were included in the structure factor calculations at idealized positions with the aid of a riding model. The SHELX-97 programs,[22] available in the WinGX package,[23] were used for structure solution and refinement. The ORTEX6a package[24] was used for molecular graphics. Selected crystal and refinement data are listed in Table 4.

CCDC-686248 (for **1**·0.5 $C_6H_5CH_3$), -686249 (for **2**·$C_6H_5CH_3$·0.5 CH_3CN), -686250 (for **3**), -686251 (for **4**·CH_3CN), -686252 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Figures containing the molecular structures of **1**, **2** and **4** (Figures S1, S2 and S3) and Scheme S1.

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