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Ruthenium Hydride Complexes with Zwitterionic Quinonoid Ligands – Isomer Separation, Structural Properties, Electrochemistry, and Catalysis

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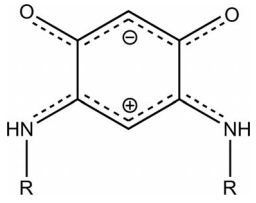
Reactions of $[Ru(PPh_3)_3(CO)(H)Cl]$ with the zwitterionic *p*-benzoquinonemonoimine-type ligands 4-(*n*-butylamino)-6-(*n*-butylimino)-3-oxocyclohexa-1,4-dien-1-olate (**Q^1**), 4-(isopropylamino)-6-(isopropylimino)-3-oxocyclohexa-1,4-dien-1-olate (**Q^2**), and 4-(benzylamino)-6-(benzylimino)-3-oxocyclohexa-1,4-dien-1-olate (**Q^3**) in the presence of a base led to the formation of mononuclear complexes $[Ru(PPh_3)_2(CO)(H)(\mathbf{Q^1}_{-H})]$ (**1a** and **1b**), $[Ru(PPh_3)_2(CO)(H)(\mathbf{Q^2}_{-H})]$ (**2a** and **2b**), and $[Ru(PPh_3)_2(CO)(H)(\mathbf{Q^3}_{-H})]$ (**3a** and **3b**), respectively. The positional isomers (**a** and **b**) that were formed in each case were separated by preparative TLC. The structural characterization of **2a** and **3a**·MeCN helped to identify the isomers, and established the distorted octahedral coordination geometry around the ruthenium center. The bond lengths in the complexes are consistent with localization of the double bonds in $\mathbf{Q^2}_{-H}$ and $\mathbf{Q^3}_{-H}$ in both their monodeprotonated and metal-coordinated forms. The Ru–C–O(carbonyl) bond angle is almost linear. Cyclic voltammetry of the complexes showed one oxidation and one reduction process. These are predominantly centered on the quinonoid ligands, which shows their redox-noninnocent character. Studies of transfer hydrogenation with **2a** as a precatalyst showed that, in the presence of KOH, acetophenone could be converted to 1-phenylethanol within 10 h in over 90 % yield.

Introduction

Quinones have fascinated chemists for decades,[1] and their interaction with transition metals has relevance to biological systems.[2–4] The redox noninnocence of such molecules imparts many interesting properties to them.[5–12] Thus, metal complexes of quinonoid ligands have been extensively investigated due to their valence ambiguity and captivating electronic structures,[13–18] their engrossing magnetic properties,[19–22] their use as bridges for molecular and supramolecular systems,[19,23–36] and in homogeneous catalysis.[37–40] In recent years, we have developed the chemistry of the potentially antiaromatic zwitterionic quinonoid ligands **Q**[41–44] (Scheme 1) and their metal complexes. Metal complexes of these ligands, where the 6π + 6π zwitterionic form is more stable than the canonical forms, have found use in homogeneous catalysis,[45,46] redox[47–49] and supramolecular chemistry,[44] and as spacers for "metal–metal coupling".[50,51]



Scheme 1. Zwitterionic quinonoid ligands.

In this work we have extended the chemistry of these zwitterionic ligands to new ruthenium hydride complexes and probed their use as catalysts for transfer hydrogenation reactions. Hydride complexes of transition metals are intermediates in a variety of useful chemical transformations.[52] The syntheses of $[Ru(PPh_3)_2(CO)(H)(\mathbf{Q^1}_{-H})]$ (**1a** and **1b**), $[Ru(PPh_3)_2(CO)(H)(\mathbf{Q^2}_{-H})]$ (**2a** and **2b**), and $[Ru(PPh_3)_2(CO)(H)(\mathbf{Q^3}_{-H})]$ (**3a** and **3b**), where **Q^1**, **Q^2**, and **Q^3** are 4-(*n*-butylamino)-6-(*n*-butylimino)-3-oxocyclohexa-1,4-dien-1-olate, 4-(isopropylamino)-6-(isopropylimino)-3-oxocyclohexa-1,4-dien-1-olate, and 4-(benzylamino)-6-(benzylimino)-3-oxocyclohexa-1,4-dien-1-olate, respectively, are presented. The separation of the positional isomers (**a** and **b** in each case) of these complexes is reported and discussed. Results obtained from elemental analysis, mass spectrometry, ^{1}H NMR and IR spectroscopy, and structural analysis have been used to establish the formulation of these metal complexes. Cyclic voltammetry studies have been carried out to elucidate the redox properties of these complexes. Finally, the use of these complexes as precatalysts for transfer hydrogenation is presented and explained.

Results and Discussion

Synthesis, Spectroscopy, and Structures

Q^1–**Q^3** were deprotonated by using KO*t*Bu. Reactions of these deprotonated ligands with $[Ru(PPh_3)_3(Cl)(CO)(H)]$

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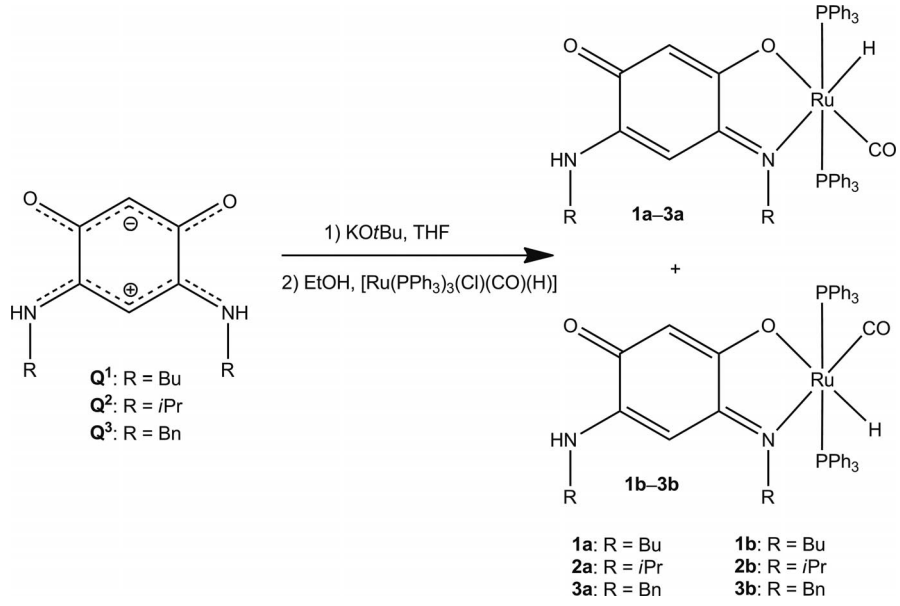


Scheme 2. Synthesis of the complexes.

under reflux conditions led to the formation of the metal complexes shown in Scheme 2.

Initial ^{1}H NMR spectroscopy (particularly the hydride signals) of the crude products indicated the formation of two different products in each case. Preparative TLC was used to separate these two fractions to obtain pure forms of **1a**–**3a**, **1b**, and **3b**. Unfortunately, the yield of **2b** was not high enough to warrant further investigation. During the reaction, one PPh_3 ligand dissociated from the precursor as a result of its high steric demand. Additionally, the chlorido ligand was abstracted as KCl with the K^+ ion associated with the deprotonated ligand. This process afforded six-coordinate, neutral ruthenium(II) complexes.

Complexes with the formula $[Ru(PPh_3)_2(CO)(H)(\mathbf{Q_{-H}})]$ can exist as various positional isomers. The ^{31}P NMR spectra of all the isolated complexes showed only one signal. Hence, the two PPh_3 ligands must be *trans* to each other, which also makes sense on steric grounds. With the two PPh_3 ligands *trans* to each other, $[Ru(PPh_3)_2(CO)(H)(\mathbf{Q_{-H}})]$ can exist as two different positional isomers, because the $\mathbf{Q_{-H}}$ ligands bind to the ruthenium center through an O and an N atom. The final identity of such isomers was established by single-crystal X-ray diffraction studies.

Complex **2a** crystallized at –10 °C from a dichloromethane solution layered with *n*-hexane (1:4), and **3a** crystallized by slow concentration of a CD_3CN solution under ambient conditions (Figures 1 and 2). Complex **2a** crystallized in the monoclinic $P2_1/n$ space group, and **3a**·MeCN crystallized in the triclinic $P\bar{1}$ space group. Crystallographic details are given in Table 4, and selected bond lengths and bond angles are listed in Table 1.

In both complexes, the ruthenium center is in a distorted octahedral environment and is coordinated by the O and N atoms of $\mathbf{Q_{-H}}$, two P atoms from PPh_3, a C atom from CO, and a hydrido ligand. The distortion from octahedral geometry is imposed by the chelating nature of $\mathbf{Q_{-H}}$ and

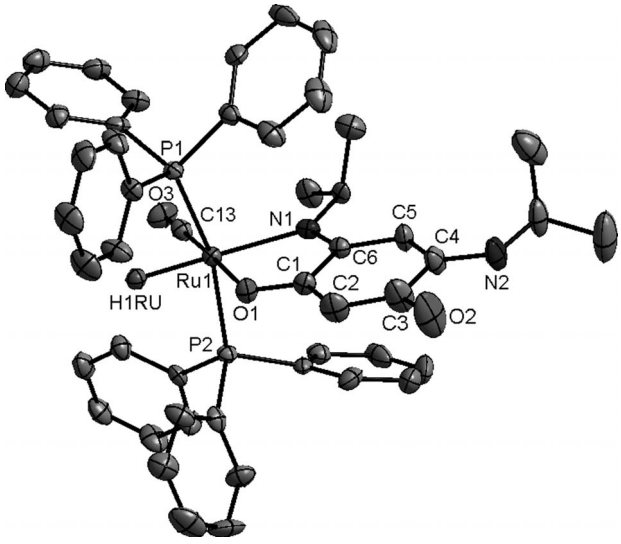


Figure 1. ORTEP plot of **2a**. Ellipsoids are drawn at 50% probability.

probably by the steric bulk of the two PPh_3 groups. Thus, the O1–Ru–N1 angle is 75.7(2) and 75.2(1)°, and the P2–Ru–P1 angle is 164.1(1) and 158.0(1)° in **2a** and **3a**·MeCN, respectively. The CO ligand in **2a** and **3a**·MeCN is *trans* to the O atom of $\mathbf{Q_{-H}}$. Hence, the identity of the red isomers **2a** and **3a**·MeCN was unambiguously established from the structural data. Extrapolation of these results to the red **1a** and the yellow **1b**–**3b** also helped to determine their identity.

Inspection of the bond lengths within $\mathbf{Q_{-H}}$ in **2a** and **3a**·MeCN shows that the C1–O1 distances of 1.276(8) and 1.290(3) Å are slightly longer than the C3–O2 distances of 1.263(9) and 1.244(3) Å, respectively. Accordingly, the C1–C2 distances of 1.398(10) and 1.382(3) Å for **2a** and **3a**·MeCN are slightly shorter than the C2–C3 distances of

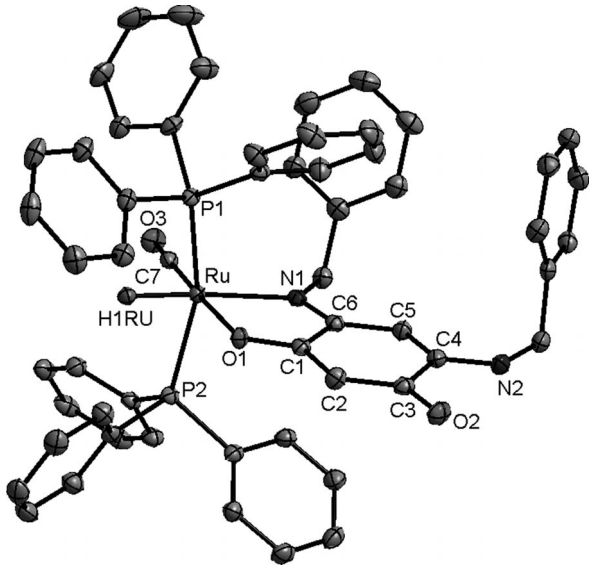


Figure 2. ORTEP plot of **3a**·MeCN. Ellipsoids are drawn at 50% probability.

Table 1. Selected bond lengths [Å] and angles [°].

	2a	**3a**·MeCN
C1–C2	1.398(10)	1.382(3)
C2–C3	1.420(13)	1.420(3)
C3–C4	1.528(12)	1.510(3)
C4–C5	1.372(9)	1.368(3)
C5–C6	1.427(9)	1.428(3)
C6–C1	1.490(9)	1.504(3)
C1–O1	1.276(8)	1.290(3)
C3–O2	1.263(9)	1.244(3)
C6–N1	1.298(8)	1.307(3)
C4–N2	1.347(9)	1.340(3)
C13–O3	1.148(9)	–
C7–O3	–	1.157(3)
Ru–O1	2.107(5)	2.138(2)
Ru–N1	2.185(5)	2.153(2)
Ru–H	1.73(9)	1.54(3)
Ru–P1	2.366(2)	2.3634(6)
Ru–P2	2.345(2)	2.3428(5)
Ru–C13	1.832(8)	–
Ru–C7	–	1.817(2)
N1–Ru–O1	75.7(2)	75.2(1)
O1–Ru–H	102.0(3)	99.0(1)
H–Ru–C13	77.0(3)	–
H–Ru–C7	–	85.0(1)
C13–Ru–N1	105.4(3)	–
C7–Ru–N1	–	99.8(1)
P1–Ru–P2	164.1(1)	158.0(1)
Ru–O1–C1	116.6(4)	116.4(1)
Ru–N1–C6	114.6(4)	117.5(1)

1.420(13) and 1.420(3) Å, respectively. A look at the C–N distances shows a related trend. The C6–N1 distances of 1.298(8) and 1.307(3) Å for **2a** and **3a**·MeCN, respectively, are shorter than the C4–N2 distances of 1.347(9) and 1.340(3) Å. This pattern is also reflected in the C5–C6 distances of 1.427(9) and 1.428(3) Å for **2a** and **3a**·MeCN, respectively, which are longer than the C4–C5 distances of 1.372(9) and 1.368(3) Å. Thus, the double bonds within the $\mathbf{Q}_{-\mathbf{H}}$ ligands became localized upon metal coordination, which is in contrast to the free ligands where the double bonds are delocalized within the "upper" and "lower" parts of the molecule (Scheme 2). The C1–C6 distances of 1.490(9) and 1.504(3) Å and the C3–C4 distances of 1.528(12) and 1.510(3) Å for **2a** and **3a**·MeCN, respectively, correspond to typical C–C single bonds and are comparable to the values found in the free ligands. These results are consistent with trends found in reported mononuclear complexes with these zwitterion-derived ligands.[47,49,51] The C–O distances of the carbonyl ligand of 1.148(9) and 1.157(3) Å for **2a** and **3a**·MeCN, respectively, are consistent with a C≡O triple bond. This is also reflected in the nearly linear Ru–C–O(carbonyl ligand) angle of 178.2 and 176.8° for **2a** and **3a**·MeCN, respectively.

In **3a**·MeCN, the phenyl rings of the benzyl groups are perpendicular to the plane of the benzoquinonemonoimine ring as well as perpendicular to each other. If we consider a plane that passes through C2 and C5 that is perpendicular to the plane containing the benzoquinonemonoimine ring, then the phenyl ring on the noncoordinated side of the ligand is parallel to this plane and that on the coordinated side is perpendicular to it. This probably happens to reduce the steric hindrance between the phenyl ring of the benzyl substituents and those of the PPh_3 group.

The positional isomers show significant differences in their ^{1}H NMR and IR spectroscopic signatures. The C–O stretching vibration for the carbonyl ligand attached to the ruthenium center appears at 1911 cm^{-1} for **1a** and at 1920 cm^{-1} for **1b** (Figure S1). A similar trend is also seen in **3a/3b** and **2a** (see Exp. Sect.). The CO ligand is *trans* to the O donor of $\mathbf{Q}^{\mathbf{1}}_{-\mathbf{H}}$ in **1a** and to the N donor in **1b** (Scheme 1). Structural analyses have shown that the donor atoms in the quinonoid ligands in their monometalated forms are best described as an O$^-$ and a neutral imine N atom. A negatively charged O$^-$ atom is expected to be a better π donor than a neutral imine N atom. Hence, in the case of **1a**, backbonding from the ruthenium center to the carbonyl ligand is larger than that in **1b**, which results in a lower carbonyl stretching frequency in **1a** than **1b**.

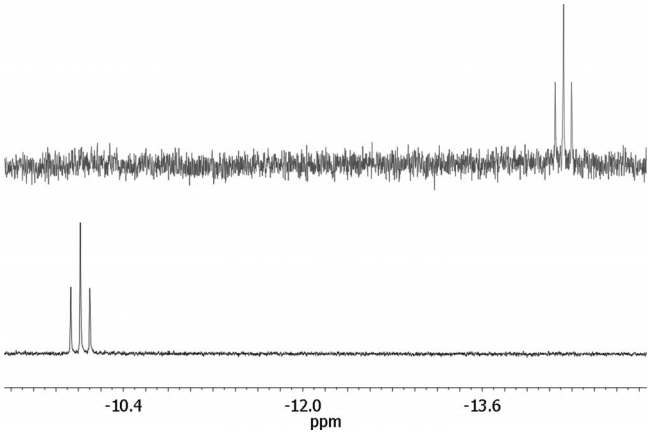


Figure 3. ^{1}H NMR (hydride region) spectra of **3a** (bottom) and **3b** (top).

The influence of the different local electronic structures in the two positional isomers is also seen in the chemical shifts of the hydride in their ^{1}H NMR spectra. Thus, the hydride resonance appears at δ = –10 and –14.53 ppm in the spectra of **3a** and **3b**, respectively (Figure 3). Both signals are triplets because of coupling with the two equivalent P nuclei of PPh_3. In the case of **3b**, the hydrido ligand is *trans* to the better π-donating O^- donor. Because of the reasons stated above, its resonance shifts to higher fields compared to that of **3a**. Similar trends are also observed for the isomers of the other complexes (see Exp. Sect.).

Cyclic Voltammetry

The presence of a redox-active ruthenium center as well as a redox-active noninnocent quinonoid ligand provides an opportunity to probe the electron-transfer properties of the complexes. Cyclic voltammetry was carried out on **1a**–**3a**, **1b**, and **3b** in CH_2Cl_2/Bu_4NPF_6 (0.1 M). All the complexes show one oxidation and one reduction step, both of which are electrochemically and chemically irreversible at 295 K at all studied scan rates (50–1000 mV/s). The irreversibility of the processes is probably related to the presence of the hydrido ligand on the ruthenium center and the acidic N–H group in the $\mathbf{Q_{-H}}$ ligands. On lowering the temperature to 223 K, the reduction step became reversible, which can be seen from the peak separation of the forward and reverse waves and their heights (Figure 4). However, the oxidation step remained irreversible, and one can see further follow-up peaks on the anodic side (not shown in Figure 4), which are probably an effect of the first oxidation step.

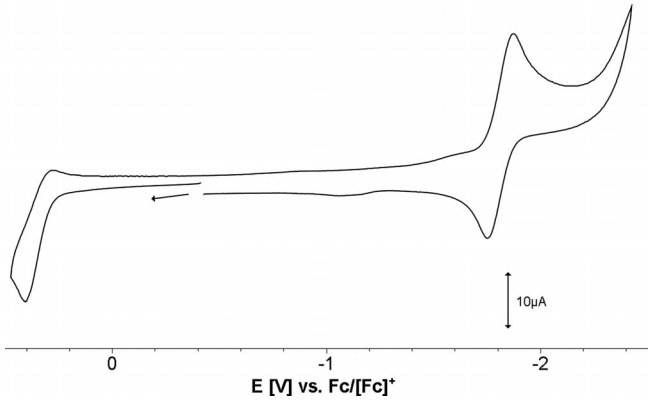


Figure 4. Cyclic voltammogram of **2a** in CH_2Cl_2/Bu_4NPF_6 (0.1 M) at 223 K. Scan rate: 100 mV/s.

The redox potentials for **1a**, **1b**, and **2a** are comparable, which is to be expected because of the similar electronic properties of the *n*-butyl and isopropyl groups. Positional isomers are also known to show virtually identical responses in their cyclic voltammograms. In contrast, the redox potentials of **3a** and **3b** are positively shifted compared to those of the other complexes (Table 2), which is expected because of the larger +I effect of *n*-butyl and isopropyl groups compared to the benzyl group. As the redox processes were not reversible at room temperature, our instrumental set up did not allow us to carry out detailed spectroelectrochemical measurements on these systems. In the absence of such data we can only speculate on the site of electron transfer in comparison to systems reported in the literature. The reduction step can be safely assigned to a reduction that predominantly takes place on $\mathbf{Q_{-H}}$. Metal complexes reported with such ligands usually show reduction steps at relatively high negative potentials.[47–49,51] Additionally, the free forms of such ligands also display such reduction processes.[47] Assignment of the oxidation step is more tricky because of the presence of the redox-active ruthenium(II) center and the noninnocent $\mathbf{Q_{-H}}$ ligands. Both these entities are known to undergo oxidation processes at comparatively low potentials.[51] As the oxidation step is irreversible even at low temperatures, one is tempted to assign it to an oxidation of the $\mathbf{Q_{-H}}$ ligand. However, we cannot totally rule out the oxidation of the ruthenium(II) center or a mixed situation.

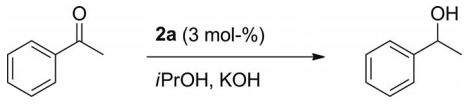
Table 2. Redox potentials [V] obtained from cyclic voltammetry experiments.[a]

Complex	E_{pa} (ox)	$E_{1/2}$(red)
1a	0.32	–1.90
1b	0.35	–1.85
2a	0.40	–1.85
3a	0.55	–1.70
3b	0.57	–1.72

[a] Potentials vs. Fc/Fc^+. From measurements in CH_2Cl_2/Bu_4NPF_6 (0.1 M).

Catalytic Transfer Hydrogenation

Ruthenium hydride complexes are intermediates in many catalytic processes,[52] and transfer hydrogenation is an important example of such a process.[53] This reaction continues to attract considerable interest for both academic and industrial applications, because it allows hydrogenation without the use of H_2 gas.[54–64] In order to test the utility of our ruthenium hydride complexes as catalysts in the transfer hydrogenation reaction, we chose **2a** because of its relatively high yield compared to that of the other complexes. Acetophenone was chosen as the substrate and 2-propanol as the hydride source. The reaction is shown in Scheme 3.



Scheme 3. Transfer hydrogenation reaction catalyzed by **2a**.

Initial attempts to perform the reaction without a base failed at room temperature as well as at a higher temperature. However, in the presence of excess base, 93% conversion to 1-phenylethanol was observed when the reaction was carried out at 70 °C (Table 3).

Table 3. Results of catalytic experiments.

Catalyst	Base	Temperature	Time	Conversion
2a	–	r.t.	15 h	–
2a	–	80 °C	15 h	2%
2a	KOH	r.t.	15 h	0%
2a	KOH	70 °C	5 h	82%
2a	KOH	70 °C	10 h	93%

The question arises as to which mechanism this reaction follows. The outer-sphere and the inner-sphere mechanisms are both well established for transfer hydrogenation catalysis.[65–67] It is also known that the distinction between the two mechanisms is sometimes not straightforward.[68] Because of the presence of an additional N–H group in $\mathbf{Q}_{-H}$, it is tempting to propose an outer-sphere mechanism that follows a Noyori-type metal–ligand bifunctional route.[53] The required amide could be generated by an internal tautomeric transformation from a predominant *p*-benzoquinonemonoimine form to an *o*-benzoquinonemonoimine form. However, the experimental conditions that were used here point to an inner-sphere mechanism because of the high temperature that is required for the catalysis to proceed. This is probably related to the generation of a free coordination site at the ruthenium center by the dissociation of a PPh_3 ligand, for example. Addtionally, excess KOH is required for the catalysis to work well, which points to the requirement of a certain concentration of 2-propanolate for the catalysis to occur. Finally, the fact that the hydrido ligand is *trans* to the possible amide site in **2a** is not in favor of an outer-sphere metal–ligand bifunctional mechanism. Although the mechanism remains to be clarified in detail, with the present data we would like to propose an inner-sphere mechanism for the transfer hydrogenation reaction.

Conclusions

We have reported the mononuclear ruthenium hydride complexes of noninnocent quinonoid ligands derived from zwitterions that are characterized by 6π + 6π delocalized systems. The positional isomers of these complexes were separated for each of the complexes. Structural data helped to unambiguously establish isomer identity and showed the relocalization of the π systems within the quinonoid ligands, which resulted in the alternation of single and double bonds. Correlations could be made between local electronic effects and the carbonyl stretching frequencies in the IR spectra as well as the hydride chemical shifts observed in the ^{1}H NMR spectra of the isomers. The complexes show one oxidation and one reduction processes in their cyclic voltammograms, both of which are tentatively assigned to electron-transfer steps on the quinonoid ligands. One of the complexes was tested for its activity as a catalyst precursor in the transfer hydrogenation reaction of acetophenone, for which it shows good activity. Initial studies of the reaction conditions point to a possible inner-sphere mechanism for this reaction. However, detailed description of the reaction steps will have to await elaborate mechanistic studies.

Experimental Section

General Considerations: All commercially available reagents were used as received. Solvents were dried and distilled according to standard procedures. The syntheses of the organic compounds were carried out under air, and the ruthenium complexes were synthesized under argon. $\mathbf{Q^1}$–$\mathbf{Q^3}$[47]and $[Ru(PPh_3)_3(CO)(H)(Cl)]$[69] were prepared according to literature procedures.

Instrumentation: The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded with a Bruker AC 250 spectrometer. Elemental analysis was performed with a Perkin–Elmer Analyzer 240. Mass spectrometry experiments were carried out with a Bruker Daltronics Mictrotof-Q mass spectrometer. IR spectra were obtained with a Nicolet 6700 FTIR instrument. Cyclic voltammetry was carried out in Bu_4NPF_6 (0.1 M) solutions by using a three-electrode configuration (glassy carbon working electrode, Pt counter electrode, Ag wire as psuedo-reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as the internal reference. For the catalytic conversions and yields, a gas chromatograph 7890A from Agilent technologies was used.

Syntheses

$[RuH(CO)(PPh_3)_2(Q^1_{-H})]$ (1a and 1b): $\mathbf{Q^1}$ (1 equiv., 0.1 mmol, 0.025 g) and KO*t*Bu (1 equiv., 0.1 mmol, 0.011 g) were mixed in a Schlenk flask under argon. To the mixture was added dry tetrahydrofuran (THF, 10 mL), and it was stirred at room temperature for 12 h. The violet solution turned orange, and an orange precipitate was formed. After 12 h, the THF was evaporated under high vacuum, and the solid dried under high vacuum for 30 min. $[Ru(PPh_3)_3(CO)(H)(Cl)]$ (1 equiv., 0.1 mmol, 0.095 g) was added to the orange solid followed by dry ethanol (20 mL). The mixture was heated to reflux under Ar overnight. The ethanol was evaporated under high vacuum. The solid was dissolved in CH_2Cl_2 (2 mL) in air and purified by preparative alumina TLC using 25% MeCN in CH_2Cl_2 as eluent. After purification, a red and a yellow fraction were obtained, which were identified as the positional isomers in a red/yellow ratio of 7:3. The overall yield was 30%. **1a** (red fraction): ^{1}H NMR (250 MHz, CD_3CN): δ = 7.64–7.57 (m, 12 H), 7.45–7.33 (m, 18 H), 5.97 (t, J = 5.75 Hz, 1 H), 4.79 (s, 1 H), 4.75 (s, 1 H), 3.04 (q, J = 6.5 Hz, 2 H), 2.90 (t, J = 8.5 Hz, 2 H), 1.62–1.51 (m, 3 H), 1.42–1.29 (m, 3 H), 1.07–0.85 (m, 7 H), 0.68 (t, J = 6 Hz, 3 H), –10.01 (t, J = 21.25 Hz, 1 H) ppm. ^{31}P{^{1}H} NMR (120 MHz, $CDCl_3$): δ = 43.5 ppm. MS: m/z = 905.2 $[M]^+$. $C_{51}H_{53}N_2O_3P_2Ru$ (905.26): calcd. C 67.76, H 5.80, N 3.10; found C 68.33, H 5.50, N 3.24. IR: $\tilde{\nu}$ = 3054 (w), 2958 (w), 2923 (w), 2362 (br.), 1911 (vs), 1735 (s), 1555 (s), 1497 (s), 1480 (s), 1090 (s) cm^{-1}. **1b** (yellow fraction): ^{1}H NMR (250 MHz, CD_3CN): δ = 7.75–6.95 (m, 70 H), 6.22 (t, J = 6.25 Hz, 1 H), 4.88 (s, 1 H), 4.5 (s, 1 H), 3.00 (q, J = 6.75 Hz, 2 H), 2.32 (t, J = 7.38 Hz, 2 H), 1.60–1.47 (m, 4 H), 1.41–1.31 (m, 4 H) 1.01–0.82 (m, 8 H), 0.59 (t, J = 7.25 Hz, 3 H), –14.32 (t, J = 17.5 Hz, 1 H) ppm. ^{31}P{^{1}H}NMR (120 MHz, CD_3CN): δ = 43.6 ppm. MS: m/z = 905.2 $[M]^+$. $C_{51}H_{53}N_2O_3P_2Ru$ (905.26): calcd. C 67.76, H 5.80, N 3.10; found C 66.95, H 5.94, N 2.99. IR: $\tilde{\nu}$ = 3055 (w), 2954 (s), 2924 (s), 2853 (br.), 1921 (vs), 1735 (s), 1495 (s), 1481 (s), 1433 (s), 1091 (s) cm^{-1}.

$[RuH(CO)(PPh_3)_2(Q^2_{-H})]$ (2a and 2b): $\mathbf{Q^2}$ (1 equiv., 0.1 mmol, 0.022 g) and KO*t*Bu (1 equiv., 0.1 mmol, 0.011 g) were mixed in a Schlenk flask under argon. To the mixture was added dry THF

(10 mL), and it was stirred at room temperature for 12 h. The violet solution turned orange, and an orange precipitate was obtained. After 12 h, the THF was evaporated under high vacuum, and the residue was dried under high vacuum for 30 min. $[Ru(PPh_3)_3(CO)(H)(Cl)]$ (1 equiv., 0.1 mmol, 0.095 g) was added to the orange solid followed by dry ethanol (20 mL). The mixture was heated to reflux overnight under Ar. The ethanol was evaporated under high vacuum. The reddish solid was dissolved in CH_2Cl_2 (2 mL) in air and purified by preparative alumina TLC using 25% MeCN in CH_2Cl_2 as eluent. Two fractions were obtained, a red and a yellow fraction, which were identified as positional isomers in a ratio of 100:1. Because of the extremely low yield of the yellow fraction (**2b**) it was not possible to characterize it. The overall yield of both isomers was 35%. **2a** (red fraction): ^{1}H NMR (250 MHz, CD_3CN): δ = 7.53–7.45 (m, 13 H), 7.33–7.25 (m, 17 H), 5.83 (d, J = 7.5 Hz, 1 H), 5.02 (s, 1 H), 4.86 (s, 1 H), 3.59 (sept, J = 6.25 Hz, 1 H), 3.42 (sept, J = 6.5 Hz, 1 H), 1.19 (d, J = 6.25 Hz, 6 H), 0.77 (d, J = 6.5 Hz, 6 H), –10.75 (t, J = 22.5 Hz, 1 H) ppm. $^{31}P\{^1H\}$ NMR (120 MHz, CD_3CN): δ = 40.4 ppm. MS: m/z = 876.2 $[M]^+$. $C_{49}H_{49}N_2O_3P_2Ru$ (876.23): calcd. C 67.19, H 5.52, N 3.20; found C 66.76, H 5.35, N 3.07. IR: $\tilde{\nu}$ = 3054 (w), 2968 (w), 2928 (w), 2361 (br.), 1909 (vs), 1732 (s), 1579 (s), 1493 (s), 1433 (s), 1277 (s), 1090 (s) cm^{-1}. **2b** (yellow fraction, not isolated): ^{1}H NMR (250 MHz, CD_3CN): δ = 7.55–7.42 (m, 13 H), 7.33–7.28 (m, 17 H), 5.83 (d, J = 7.5 Hz, 1 H), 5.15 (s, 1 H), 4.78 (s, 1 H), 3.53 (sept, J = 6.25 Hz, 1 H), 3.38 (sept, J = 6.5 Hz, 1 H), 1.19 (d, J = 6.25 Hz, 6 H), 0.77 (d, J = 6.5 Hz, 6 H), –14.52 (t, J = 17.5 Hz, 1 H) ppm. $^{31}P\{^1H\}$ NMR (120 MHz, CD_3CN): δ = 41.5 ppm.

$[RuH(CO)(PPh_3)_2(Q^3_{-H})]$ (3a and 3b): Q^3 (1 equiv., 0.1 mmol, 0.032 g) and KO*t*Bu (1 equiv., 0.1 mmol, 0.011 g) were mixed in a Schlenk flask under argon. To the mixture was added dry THF (10 mL), and it was stirred at room temperature for 12 h. The violet solution turned orange, and an orange precipitate was obtained. After 12 h, the THF was evaporated under high vacuum, and the residue was dried under high vacuum for 30 min. $[Ru(PPh_3)_3(CO)(H)(Cl)]$ (1 equiv., 0.1 mmol, 0.095 g) was added to the orange solid followed by dry ethanol (20 mL). The mixture was heated to reflux under Ar overnight. The ethanol was evaporated under high vacuum. The reddish solid was dissolved in CH_2Cl_2 (2 mL) in air and purified by preparative alumina TLC using 25% MeCN in CH_2Cl_2 as eluent. Two fractions were obtained, a red and a yellow one, which were identified to be positional isomers in a red/yellow ratio of 7:3. The overall yield was 37%. **3a** (red fraction): ^{1}H NMR (250 MHz, CD_3CN): δ = 7.42–7.25 (m, 36 H), 7.07 (t, J = 7.5 Hz, 2 H), 6.84 (t, J = 7.5 Hz, 2 H), 6.63 (d, J = 7.5 Hz, 2 H), 5.12 (s, 1 H), 4.84 (s, 1 H), 4.36 (d, J = 6.5 Hz, 2 H), 4.05 (s, 2 H), –10.00 (t, J = 22.5 Hz, 1 H) ppm. $^{31}P\{^1H\}$ (120 MHz, CD_3CN): δ = 41.5 ppm. MS: m/z = 973.2 $[M]^+$. $C_{57}H_{49}N_2O_3P_2Ru$ (973.26): calcd. C 70.43, H 4.98, N 2.88; found C 70.13, H 5.05, N 2.77. IR: $\tilde{\nu}$ = 3057 (w), 2955 (s), 2924 (s), 2853 (s), 2360 (s), 2342 (s), 1915 (vs), 1735 (s), 1556 (s), 1258 (s), 1091 (br.), 1009 (br.) cm^{-1}. **3b** (yellow fraction): ^{1}H NMR (250 MHz, CD_3CN): δ = 7.70–7.24 (m, 35 H), 6.92 (d, J = 7.25 Hz, 3 H), 6.54 (t, J = 7.25 Hz, 3 H), 4.80 (s, 1 H), 4.78 (s, 1 H), 4.38 (d, J = 6.25 Hz, 2 H), 3.8 (s, 2 H), –14.53 (t, J = 17.25 Hz, 1 H) ppm. $^{31}P\{^1H\}$ NMR (120 MHz, CD_3CN): δ = 43.1 ppm. MS: m/z = 973.2 $[M]^+$. $C_{57}H_{49}N_2O_3P_2Ru$ (973.26): C 70.43, H 4.98, N 2.88; found C 70.18, H 4.86, N 2.75. IR: $\tilde{\nu}$ = 2959 (s), 2925 (s), 2216 (w), 2127 (w), 1926 (vs), 1736 (vs), 1436 (s), 1258 (s), 1091 (br.), 1006 (br.) cm^{-1}.

General Procedure for the Catalysis: The catalyst (0.03 equiv., 0.015 mmol, 0.013 g) was dissolved in 2-propanol (5 mL) and the mixture stirred for 5 min. KOH (0.33 equiv., 0.17 mmol, 0.009 g) was added, and the mixture was stirred for 5 min. Acetophenone (1 equiv., 0.5 mmol, 0.061 g), dissolved in 2-propanol (5 mL), was added. The mixture was and stirred under Ar at 70 °C for 5 h or overnight. After completion of the reaction, the mixture was filtered through cotton wool, and the conversion was analyzed by gas chromatography.

X-ray Crystallography: Data collection was performed with a Kappa CCD diffractometer. The measurements were carried out at 173 K by using Mo-K_α radiation (graphite monochromator). The structures were solved and refined by full-matrix least-squares techniques on F^2 with SHELX-97.[70] A severe disorder of the solvent was observed in **2a**; attempts to model the disorder failed. A SQUEEZE procedure[71] was applied on 586 Å^3 of solvent-accessible voids and 286 e/cell. The acetonitrile molecules in **3a** are disordered (Table 4). CCDC-804975 (for **2a**) and -804977 (for **3a**) 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 footnote on the first page of this article): IR spectra of the complexes.

Table 4. Crystallographic details.

	2a	**3a**·MeCN
Empirical formula	$C_{49}H_{48}N_2O_3P_2Ru$	$C_{60}H_{49}N_3O_3P_2Ru$
M_r	875.90 g mol^{-1}	1013.03 g mol^{-1}
Crystal system, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
a, b, c [Å]	12.2122(7), 15.6578(5), 13.9000(8)	13.1210(3), 13.5752(2), 15.7258(4)
α, β, γ [°]	90, 108.663(3), 90	112.9880(10), 98.2500(10), 103.0220(10)
V [Å^3]	2518.1(2)	2427.20(9)
Z	2	2
Density [g cm^{-3}]	1.155	1.386
F(000)	908	1048
Radiation type	Mo-K_α	Mo-K_α
μ [mm^{-1}]	0.412	0.439
Crystal size	0.25 × 0.15 × 0.15 mm	0.25 × 0.10 × 0.15
Measured reflections	6433	20522
Independent reflections	3524	11556
Observed [$I > 2\sigma(I)$] reflections	4857	10301
R_{int}	0.0789	0.0380
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0545, 0.1483, 1.070	0.0296, 0.1092, 1.177
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	0.589, –1.047	0.573, –1.272

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