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Note

Synthesis and properties of carboxy-substituted half-sandwich ruthenium complexes with chelating bisphosphine ligands (η^5-$C_5H_4CO_2H$)Ru(η^2-L)X (X = I, H)

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Abstract

Several Ru(II) complexes (η^5-$C_5H_4CO_2H$)Ru(η^2-L)I have been prepared by the hydrolysis of the ester linkage in (η^5-$C_5H_4CO_2$-*t*-Bu)Ru(η^2-L)Cl with trimethylsilyl iodide. The hydrides (η^5-$C_5H_4CO_2H$)Ru(η^2-L)H may be prepared by reduction of the iodide complexes in KOH/MeOH solutions followed by acidification. Complexes with several chelating bisphosphine ligands have been prepared in this way. The carboxylate anions [(η^5-$C_5H_4CO_2$)Ru(η^2-L)H]$^-$ are readily protonated by weak acids to give the carboxyCp complexes. The pK_a of the carboxy proton of (η^5-$C_5H_4CO_2H$)Ru(dppe)H (dppe = 1,2-bis(diphenylphosphino)ethane) is 11.3 in DMSO. Protonation of the neutral hydride complex (η^5-$C_5H_4CO_2H$)Ru(dppf)H gives the cationic dihydride (η^5-$C_5H_4CO_2H$)Ru(dppf)H_2^+; the dihydride structure has been confirmed by measuring the T_1 of its ^{1}H NMR hydride resonance over a range of temperatures. The oxidations of the halide complexes (η^5-$C_5H_4CO_2H$)Ru(dppf)I and (η^5-$C_5H_4CO_2$*t*-Bu)Ru(dppf)Cl (dppf = 1,1′-bis(diphenylphosphino)ferrocene) have been studied by cyclic voltammetry.

Keywords: Ruthenium hydrides; Ester hydrolysis; Carboxy complexes

1. Introduction

Although many complexes with functionalized cyclopentadienyl ligands are known [1], those with carboxy substituents ($C_5H_4CO_2H$ complexes) have not been studied extensively. They should be soluble in aqueous base, allowing catalysts to function in aqueous or biphasic environments. They should be good electrochemical and spectroscopic probes when the carboxy group is attached covalently to biomolecules [2].

Three routes to $C_5H_4CO_2H$ complexes have been reported: (a) Cp ligands can be lithiated and treated with CO_2 [3], (b) $C_5H_4CO_2Me$ complexes can be prepared and the ester saponified [4], and (c) $C_5H_4CO_2H$ complexes can be prepared directly from the free ligand (Thiele's acid) [5,6]. However, we have found that none of these methods work for the preparation of (η^5-$C_5H_4CO_2H$)Ru(η^2-L)X (Table 1), so we have tried a variant of (b) that avoids strong base: the preparation of complexes of the corresponding *t*-butyl esters and the use of trimethylsilyl iodide to effect their hydrolysis [7].

2. Results and discussion

2.1. Synthesis

The first step (lithiation of a Cp ligand) of approach (a) is sometimes possible in the presence of a hydride ligand: for example, the ring is the kinetic site of lithiation of CpRe(NO)(PPh_3)H with *n*-BuLi/$Me_2NCH_2CH_2NMe_2$ at −70 °C [8]. However, approach (a) proved successful with neither CpRu(CO)$_2$H nor CpRu(dppe)H. We then tried approach (b), after preparing (η^5-$C_5H_4CO_2Me$)Ru(dppe)X

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Table 1
(η^5-C_5H_4R)Ru(L)X complexes

Complex	X	R	L
3	Cl	CO_2t-Bu	$(PPh_3)_2$
4a	Cl	CO_2t-Bu	dppe
4c	Cl	CO_2t-Bu	dppf
5a	I	CO_2H	dppe
5b	I	CO_2H	*S*,*S*-CHIRAPHOS
5c	I	CO_2H	dppf
7a	H	CO_2H	dppe
7b	H	CO_2H	*S*,*S*-CHIRAPHOS
7c	H	CO_2H	dppf
8a	H	CO_2^-	dppe
9a	H	CO_2t-Bu	dppe
9c	H	CO_2t-Bu	dppf

(X = Cl, H) [9]. However, numerous attempts to hydrolyze this methyl ester (aqueous base and methanol, acetone, or THF) failed, as did an attempt to hydrolyze the ester linkage in (η^5-$C_5H_4CO_2Me$)$Ru(PPh_3)_2Cl$ with trimethylsilyl iodide. (Trimethylsilyl iodide can be used to hydrolyze some methyl esters, although the reactions are often slow [7].) We then tried approach (c), but were unable to prepare $C_5H_4CO_2H$ complexes by the reaction of Thiele's acid with $Ru_3(CO)_{12}$ or $RuCl_3 \cdot 3H_2O$/phosphines [10].

Eventually we made the bis(triphenylphosphine) ruthenium chloride complex **3** by treating $RuCl_2(PPh_3)_3$ (**1**) with Li[$C_5H_4CO_2t$-Bu] (**2**) [11] in refluxing THF (Scheme 1). Treating **3** with dppe in refluxing toluene replaced the triphenylphosphines with dppe, giving the *t*-butyl ester chloride complex **4a**. Treating **4a** with NaOMe in MeOH gave (η^5-$C_5H_4CO_2t$-Bu)Ru(dppe)H (**9a**). The latter decomposed under the acidic conditions (aqueous HCl/CH_2Cl_2) needed to hydrolyze the ester, but gave **5a** when treated with excess trimethylsilyl iodide followed by water. We therefore treated **4a** with excess trimethylsilyl iodide in CH_2Cl_2, and found that it also gave **5a** after treatment with water [7]. The exchange of chloride with iodide is not surprising given the lability of halide ligands in such complexes [12].

Refluxing **5a** with KOH in methanol afforded a light yellow solution of the $C_5H_4CO_2^-$ hydride complex **6a** (Scheme 2). The addition of benzoic acid gave the carboxy complex **7a** in solution, while the addition of benzamidine hydrochloride gave the salt **8a**. Both hydride complexes precipitated after the addition of water.

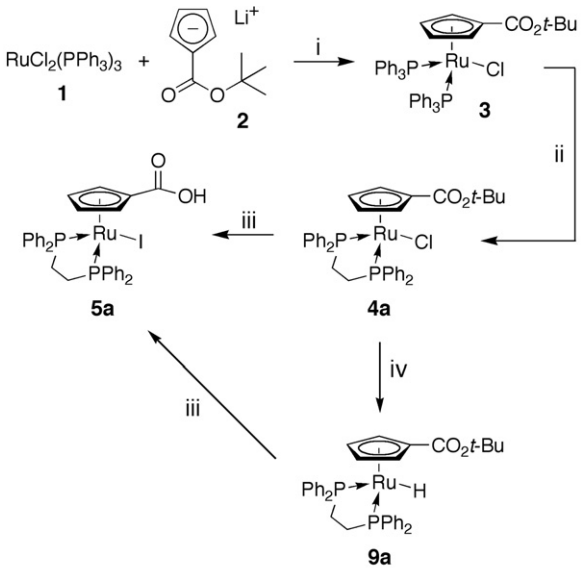
These methods have proven readily adaptable to Ru complexes of other bisphosphines. The complexes in Table 1 have all been prepared by procedures like those in Schemes 1 and 2.

2.2. Properties and reactivity

Although their analogs with unsubstituted cyclopentadienyl ligands are quite soluble in CH_2Cl_2, the orange-red $C_5H_4CO_2H$ ruthenium iodides **5a**, **5b**, and **5c** are much more soluble in DMSO than in halogenated solvents (the iodide **5a** is only sparingly soluble in methylene chloride). The difference is presumably the result of hydrogen bonding between the carboxy substituents and DMSO [13]. The yellow hydrides (**7a**, **7b**, **7c**, and **8a**) behave similarly. None of the carboxyCp complexes are particularly sensitive to oxygen; in the solid state they can be handled in air.

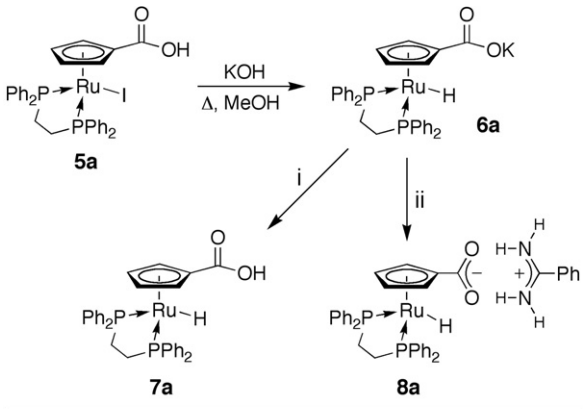
The ^1H NMR spectra of the carboxyCp complexes **5** and **7** in DMSO-d_6 all display broad peaks that range from δ 11.43 to 12.49 for their carboxy protons. The hydride ligands in **7** show well-resolved triplets that range from δ −13.96 to −12.75, with no evidence of any interaction between these ligands and the carboxy protons (at least in DMSO).

Treatment of the benzamidinium salt **8a** with 1 equiv. of $HBF_4 \cdot OMe_2$ in DMSO-d_6 gave only the carboxyCp com-



i. THF, Δ
ii. dppe, PhMe, Δ
iii. (1) Me_3SiI, CH_2Cl_2 (2) H_2O
iv. NaOMe, MeOH, Δ

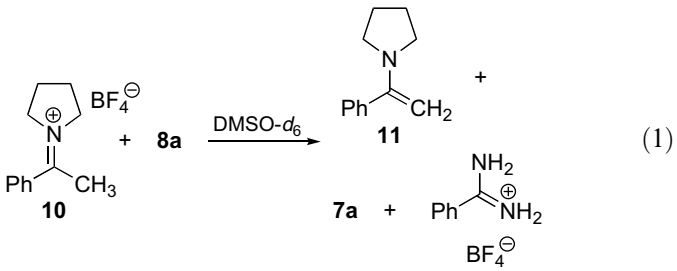
Scheme 1.



i. benzoic acid, H_2O
ii. benzamidine hydrochloride, H_2O

Scheme 2.

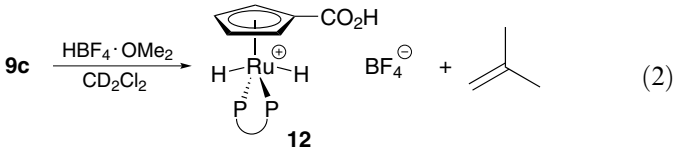
plex **7a** and benzamidinium tetrafluoroborate. Treatment of **8a** with a weaker acid, the pyrrolidinium cation **10**, also gave **7a** along with the enamine **11** (Eq. (1)). Clearly in DMSO the carboxylate of **8a** is more basic than the hydride ligand.



(1)

By treating **7a** with various amines in DMSO-d_6 and determining the position of the equilibrium by ^{1}H NMR, we determined a pK_a of 11.3 for the carboxy proton of **7a**. The acidity of **7a** is thus comparable to that of ordinary carboxylic acids (the pK_a of benzoic acid in DMSO is 11.1) [14].

Protonation of (η^5-$C_5H_4CO_2H$)Ru(dppf)H (**7c**) or the ester complex (η^5-$C_5H_4CO_2t$-Bu)Ru(dppf)H (**9c**) with $HBF_4 \cdot OMe_2$ in CD_2Cl_2 gave a cation **12** with a triplet at δ −7.78 ($J_{P-H} = 22.2$ Hz); isobutylene[15] was formed as a byproduct (Eq. (2)). In order to determine the structure of **12**, the spin–lattice relaxation time (T_1) of its hydride resonance was determined at 300 MHz over a range of temperatures (Fig. 1). The relatively high value of the minimum T_1 (0.259(7) s at 241.6 K) indicates that **12** is a classical dihydride complex [16].



(2)

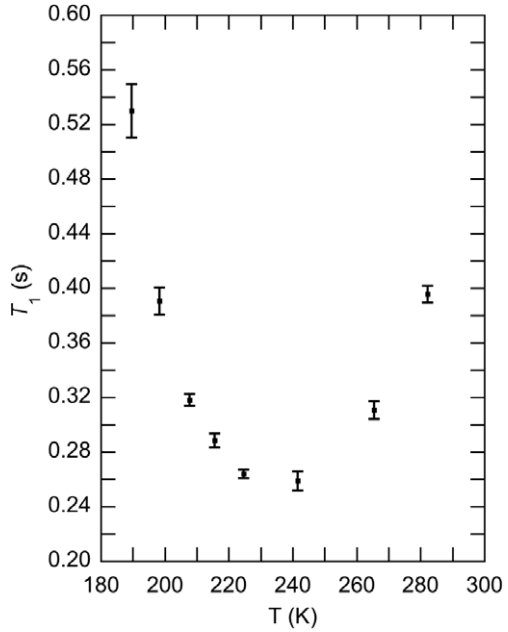


Fig. 1. T_1 of the dihydride resonance of **12** (CD_2Cl_2, 300 MHz).

The ^{1}H NMR spectrum of **12** shows only two resonances for the cyclopentadienyl protons of the dppf ligand (δ 4.31 and 4.41). This simple pattern is expected for the *trans* isomer, but not for the *cis* (Fig. 2) [17]. We therefore conclude that **12** is a *trans* dihydride complex; $[Cp^*Ru(dppf)H_2]^+$ is believed to be *trans* on the basis of a similar argument [18].

2.3. Electrochemistry of the heterobimetallic halide complexes

It is well known that carboxy and ester substituents on Cp rings are electron-withdrawing [19]. The Fe(II)/Fe(III) couples (in CH_3CN) of ferrocene carboxylic acid and ferrocene carboxylic acid ethyl ester are shifted approximately 0.24 V in the anodic direction from that of ferrocene [19].

The cyclic voltammograms of the dppf ruthenium halide complexes (Fig. 3, Table 2) show two reversible oxidations in CH_2Cl_2. For these complexes, we assign the first oxidation to Ru(II)/Ru(III) and the second to Fe(II)/Fe(III) [20]. The unsubstituted complex CpRu(dppf)Cl is the most easily oxidized of the three. The slight differences between the potentials of **4c** and **5c** result not only from the difference between CO_2H and CO_2t-Bu substitution, but also from the difference between the halide ligands (chloride should be a better donor than iodide) [21].

3. Experimental

3.1. General procedures

All air-sensitive compounds were prepared and handled under a N_2/Ar atmosphere using standard Schlenk and inert-atmosphere box techniques. Hexanes, toluene, diethyl ether, and methylene chloride were deoxygenated and dried over two successive activated alumina columns under argon. Benzene and THF were distilled from Na and benzophenone under N_2. Commercial anhydrous methanol was degassed by three freeze-pump-thaw cycles. Water was de-ionized with a Barnstead NANOpure water system and degassed by three freeze-pump-thaw cycles. CD_2Cl_2 was degassed by three freeze-pump-thaw cycles and dried over 4 Å molecular sieves. THF-d_8 was distilled from Na

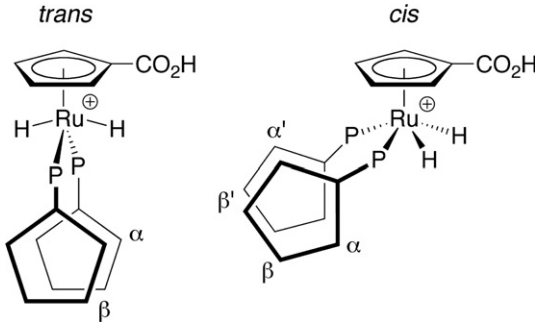


Fig. 2. The complex (η^5-$C_5H_4CO_2H$)Ru(dppf)H_2^+ as *trans* (**12**) and *cis* (not observed). The iron atom and phenyl groups of the dppf ligand have been omitted for clarity.

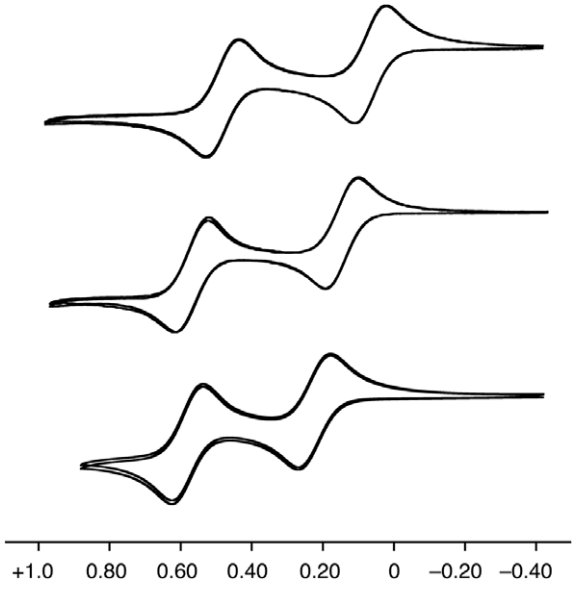


Fig. 3. Cyclic voltammograms of CpRu(dppf)Cl (top), (η^5-$C_5H_4CO_2t$-Bu)Ru(dppf)Cl (**4c**, middle), and (η^5-$C_5H_4CO_2H$)Ru(dppf)I (**5c**, bottom). Scan rate 50 mV/s. Potential (V) vs. Fc/Fc^+ in CH_2Cl_2.

Table 2
Cyclic voltammetry – heterobimetallic halide complexes

Complex	Ru(II)/Ru(III)	Fe(II)/Fe(III)
CpRu(dppf)Cl	+0.06	+0.48
(η^5-$C_5H_4CO_2t$-Bu)Ru(dppf)Cl (**4c**)	+0.15	+0.57
(η^5-$C_5H_4CO_2H$)Ru(dppf)I (**5c**)	+0.22	+0.58

Potentials ($E_{1/2}$) are in Volts vs. Fc/Fc^+ in CH_2Cl_2. Scan rate 50 mV/s.

and benzophenone under N_2. CpRu(dppf)Cl [22], 1-(1-phenylethylidene)pyrrolidinium tetrafluoroborate (**10**) [23], 1-(1-pyrrolidinyl)-1-phenylethene (**11**) [24], and $RuCl_2(PPh_3)_3$ (**1**) [25] were prepared by the methods cited.

Cyclic voltammetry was performed with a BAS CV-50W Potentiostat. The supporting electrolyte for all solutions except the reference electrode was 0.10 M $[Bu_4N]PF_6$ in CH_2Cl_2. The cell consisted of a 1.6 mm diameter platinum disk working electrode, a silver wire reference electrode (0.01 M $AgNO_3$ + 0.10 M $[Bu_4N]PF_6$ in CH_3CN), and a platinum wire auxiliary electrode (0.10 M $[Bu_4N]PF_6$ in CH_2Cl_2). Fc/Fc^+ (0.001 M in CH_2Cl_2) was used as an external reference and was found to be +0.22 V with respect to our reference electrode. All samples were prepared under a N_2/Ar atmosphere and further purged with Ar before measurement. Analyte concentrations were 0.001 M. All scans were recorded at 50 mV/s.

3.2. ^1H NMR of complexes containing monosubstituted cyclopentadienides

The protons in positions 2, 3, 4, and 5 of a monosubstituted cyclopentadienide form an AA′BB′ system in the ^1H NMR. Two apparent triplets will result if $J_{23} - J_{24}$ is small enough. In this case the observed splitting is an average, $(J_{23} + J_{24})/2 = (J_{45} + J_{35})/2$ [26]. Sometimes this splitting is too small to be observable; in these cases the A and B resonances are reported as singlets.

3.3. t-Butoxycarbonylcyclopentadienyllithium (**2**)

n-BuLi (28.8 mL, 1.6 M in hexanes, 46.1 mmol) was added slowly to *t*-butoxycarbonylcyclopentadiene[11] (6.66 g, 40.1 mmol) in Et_2O at −78 °C. The mixture was warmed to room temperature and stirred for 1 h. Hexanes were added until a white precipitate formed. The solvent was removed with a filter cannula. The solid was washed with hexanes several times and dried under vacuum to give a white powder (5.68 g, 33.0 mmol, 82% yield). ^1H NMR (400 MHz, THF-d_8): δ 1.48 (s, *t*-Bu, 9H), 5.63 (apparent t, Cp, apparent $J = 2.9$ Hz, 2H), 6.22 (apparent t, Cp, apparent $J = 2.9$ Hz, 2H). ^{13}C {^1H} NMR (100 MHz, THF-d_8): δ 29.56, 75.67, 109.59, 111.03, 112.87, 169.41.

3.4. ($C_5H_4CO_2t$-Bu)Ru(PPh_3)$_2$Cl (**3**)

A solution of **1** (2.88 g, 3.0 mmol) and **2** (0.52 g, 3.0 mmol) in 40 mL of THF was stirred at room temperature for 2 h. Addition of hexanes (100 mL) caused a red solid to precipitate. The solid was filtered, washed several times with hexanes, and dried under vacuum to afford the crude product (containing some residual LiCl) as a brick-red powder (1.97 g, 2.39 mmol) in 80% yield. Analytically pure product was obtained by passing the crude material through a pad of silica with Et_2O and evaporation of the solvent. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.60 (s, *t*-Bu, 9H), 3.43 (s, Cp, 2H), 4.64 (s, Cp, 2H), 7.12–7.37 (m, Ar, 30H). ^{31}P {^1H} NMR (161.9 MHz, CD_2Cl_2): δ 39.02. Anal. Calc. for $C_{46}H_{43}ClO_2P_2Ru$: C, 66.86; H, 5.25; Cl, 4.29. Found: C, 67.14; H, 5.37; Cl, 4.18%.

3.5. ($C_5H_4CO_2t$-Bu)Ru(dppe)Cl (**4a**)

A suspension of **3** (1.20 g, 1.45 mmol) was refluxed with 1,2-bis(diphenylphosphino)ethane (0.63 g, 1.57 mmol) in 60 mL of toluene for 18 h. The reaction mixture was cooled to room temperature and loaded on a column (230–400 mesh silica, 15 cm × 2 cm diameter). Elution of phosphines with benzene followed by elution of the product with benzene/ether (1/5) and evaporation of the solvent gave an orange powder (0.69 g, 0.99 mmol, 68% yield). ^1H NMR (400 MHz, CD_2Cl_2): δ 1.41 (s, *t*-Bu, 9H), 2.44–2.50 (m, $Ph_2PCH_2CH_2PPh_2$, 2H), 2.63–2.69 (m, $Ph_2PCH_2CH_2PPh_2$, 2H), 4.03 (s, Cp, 2H), 5.15 (s, Cp, 2H), 7.13–7.86 (m, Ar, 20H). ^{31}P {^1H} NMR (161.9 MHz, CD_2Cl_2): δ 80.63. Anal. Calc. for $C_{36}H_{37}ClO_2P_2Ru$: C, 61.76; H, 5.33; Cl, 5.06. Found: C, 61.76; H, 5.45; Cl, 5.00%.

3.6. ($C_5H_4CO_2t$-Bu)Ru(dppe)H (**9a**)

A solution of **4a** (0.35 g, 0.50 mmol) in 40 mL of MeOH was treated with 0.12 g sodium and refluxed for 18 h. The

solvent was evaporated, the residue extracted with benzene, and after filtration the bright yellow solution was evaporated to give a yellow solid. The solid was washed with MeOH several times and dried under vacuum (0.19 g, 0.29 mmol, 58% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ −13.50 (t, Ru*H*, $J_{P-H} = 34.3$ Hz, 1H), 1.36 (s, *t*-Bu, 9H), 2.02–2.50 (m, $Ph_2PCH_2CH_2PPh_2$, 4H), 4.44 (apparent t, Cp, apparent $J = 2.0$ Hz, 2H), 5.23 (apparent t, Cp, apparent $J = 2.0$ Hz, 2H), 7.30–7.71 (m, Ar, 20H). ^{31}P {^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 91.87. Anal. Calc. for $C_{36}H_{38}O_2P_2Ru$: C, 64.95; H, 5.75. Found: C, 64.65; H, 5.69%.

3.7. ($C_5H_4CO_2H$)Ru(dppe)I (**5a**)

A solution of **4a** (0.69 g, 0.99 mmol) in 50 mL of CH_2Cl_2 was stirred with trimethylsilyl iodide (0.42 mL, 2.97 mmol) for 30 min. Water (40 mL) was added and the mixture stirred overnight, then the volatile components were removed by vacuum. The product was collected by filtration, washed with 10 mL of MeOH, 10 mL of Et_2O, and 4 mL of CH_2Cl_2, then dried under vacuum to give 0.64 g of a brick-red powder (0.87 mmol, 88% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.68–2.85 (m, $Ph_2PCH_2CH_2PPh_2$, 4H), 4.18 (s, Cp, 2H), 5.19 (s, Cp, 2H), 7.07–7.84 (m, Ar, 20H), 12.22 (br, CO_2H, 1H). ^{31}P {^{1}H} NMR (161.9 MHz, DMSO-d_6): δ 79.39. Anal. Calc. for $C_{32}H_{29}IO_2P_2Ru$: C, 52.26; H, 3.97; I, 17.25. Found: C, 52.28; H, 3.84; I, 17.01%.

3.8. ($C_5H_4CO_2H$)Ru(dppe)H (**7a**)

A solution of **5a** (1.85 g, 2.52 mmol) and KOH (1.70 g, 30.3 mmol) in 50 mL of MeOH was refluxed for 18 h. The color of the mixture changed from red to light yellow during reflux. At room temperature, benzoic acid (4.07 g, 33.3 mmol) was added in one portion and the mixture was stirred for 20 min. Addition of 7 mL of water gave a yellow precipitate which was filtered and washed twice with 10 mL of water and twice with 10 mL of Et_2O. The yellow solid was dried under vacuum (1.38 g, 2.26 mmol, 90% yield). ^{1}H NMR (300 MHz, DMSO-d_6): δ −13.93 (t, Ru*H*, $J_{P-H} = 34.8$ Hz, 1H), 1.95–2.40 (m, $Ph_2PCH_2CH_2PPh_2$, 4H), 4.51 (apparent t, Cp, apparent $J = 2.1$ Hz, 2H), 5.19 (apparent t, Cp, apparent $J = 2.1$ Hz, 2H), 7.28–7.44 (m, Ar, 16H), 7.65–7.74 (m, Ar, 4H), 11.67 (br, CO_2H, 1H). ^{31}P {^{1}H} NMR (161.9 MHz, DMSO-d_6): δ 90.20. Anal. Calc. for $C_{32}H_{30}O_2P_2Ru$: C, 63.05; H, 4.96. Found: C, 62.88; H, 4.91%.

3.9. [($C_5H_4CO_2$)Ru(dppe)H][benzamidinium] (**8a**)

A solution of **5a** (0.24 g, 0.33 mmol) and KOH (0.25 g, 4.40 mmol) in 15 mL of MeOH was refluxed for 20 h. At room temperature, benzamidine hydrochloride (1.0 g, 6.39 mmol) was added in one portion and the mixture was stirred for 20 min. The volume was reduced by vacuum and the product precipitated by the addition of 35 mL of water. The yellow solid was filtered, washed with water (4 × 10 mL), and dried under vacuum (0.20 g, 0.27 mmol, 82% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ −13.96 (t, Ru*H*, $J_{P-H} = 35.0$ Hz, 1H), 1.95–2.34 (m, $Ph_2PCH_2CH_2PPh_2$, 4H), 4.35 (s, Cp, 2H), 5.13 (s, Cp, 2H), 7.28–7.38 (m, Ar, 12H), 7.41–7.50 (m, Ar, 4H), 7.56–7.60 (m, Ar, 2H), 7.65–7.68 (m, Ar, 1H), 7.73–7.80 (m, Ar, 6H). ^{31}P {^{1}H} NMR (161.9 MHz, DMSO-d_6): δ 90.16. Anal. Calc. for $C_{39}H_{38}N_2O_2P_2Ru$: C, 64.19; H, 5.25; N, 3.84. Found: C, 64.09; H, 5.35; N, 3.62%.

3.10. ($C_5H_4CO_2H$)Ru(*S,S*-CHIRAPHOS)I (**5b**)

A solution of **3** (1.41 g, 1.70 mmol) and (2*S*,3*S*)-bis(diphenylphosphino)butane (0.77 g, 1.79 mmol) in 70 mL of toluene was refluxed for 16 h. The reaction mixture was loaded on a column (230–400 mesh silica, 14 cm × 2 cm diameter). Elution of phosphines with benzene followed by elution of a red band with benzene/ether (1/5) and evaporation of the solvent gave a red solid (the ester complex). This solid was treated with trimethylsilyl iodide (0.73 mL, 5.1 mmol) in 50 mL of CH_2Cl_2 for 30 min, then 15 mL of water was added and the mixture was stirred for 20 h. Volatile components were removed by vacuum. The product, an orange powder, was filtered and washed with 6 mL of MeOH and 10 mL of Et_2O, then dried under vacuum (1.05 g, 1.38 mmol, 80% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.96–1.08 (m, CH_3, 6H), 2.13–2.25 (m, C*H*, 1H), 3.00–3.10 (m, C*H*, 1H), 3.76 (s, Cp, 1H), 4.64 (s, Cp, 1H), 4.99 (s, Cp, 1H), 5.02 (s, Cp, 1H), 6.83–6.90 (m, Ar, 2H), 7.20–7.48 (m, Ar, 14H), 7.48–7.54 (m, Ar, 2H), 7.79–7.83 (m, Ar, 2H), 12.01 (s, CO_2H, 1H). ^{31}P {^{1}H} NMR (161.9 MHz, DMSO-d_6): AB pattern, δ 78.45 (d, $J_{P-P} = 34.0$ Hz), 81.72 (d, $J_{P-P} = 34.0$ Hz). Anal. Calc. for $C_{34}H_{33}IO_2P_2Ru$: C, 53.48; H, 4.36; I, 16.62. Found: C, 53.35; H, 4.40; I, 16.38%.

3.11. ($C_5H_4CO_2H$)Ru(*S,S*-CHIRAPHOS)H (**7b**)

A solution of **5b** (0.40 g, 0.52 mmol) and KOH (0.28 g, 5.0 mmol) in 15 mL of MeOH was refluxed for 6 h. At room temperature, AcOH (0.40 mL, 7.0 mmol) was added in one portion and the mixture was stirred for 20 min. Addition of 15 mL of water gave a yellow precipitate which was filtered, washed with water (3 × 5 mL), and dried under vacuum (0.27 g, 0.42 mmol, 81% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ −13.34 (dd, Ru*H*, $J = 37.8$ Hz, $J = 27.6$ Hz, 1H), 0.62–0.82 (m, CH_3, 6H), 1.80–1.95 (br, C*H*, 2H), 4.24 (s, Cp, 1H), 4.36 (s, Cp, 1H), 4.90 (s, Cp, 1H), 4.94 (s, Cp, 1H), 7.25–7.72 (m, Ar, 20H), 11.43 (br, CO_2H, 1H). ^{31}P {^{1}H} NMR (161.9 MHz, DMSO-d_6): AB pattern, δ 92.87 (d, $J_{P-P} = 35.7$ Hz), 94.70 (d, $J_{P-P} = 35.7$ Hz). Anal. Calc. for $C_{34}H_{34}O_2P_2Ru$: C, 64.04; H, 5.37. Found: C, 63.75; H, 5.32%.

3.12. ($C_5H_4CO_2t$-Bu)Ru(dppf)Cl (**4c**) and ($C_5H_4CO_2H$)Ru(dppf)I (**5c**)

In 50 mL of toluene, **3** (1.00 g, 1.21 mmol) and 1,1′-bis(diphenylphosphino)ferrocene (0.70 g, 1.27 mmol) were refluxed for 18 h. The reaction mixture was loaded on a column (230–400 mesh silica, 18 cm × 2 cm diameter). Elution of phosphines with benzene followed by elution of a red band with benzene/ether (1/5) and evaporation of the solvent gave a red solid (**4c**) that was washed with hexanes several times and dried under vacuum. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.40 (s, *t*-Bu, 9H), 3.57 (s, Cp, 2H), 4.07 (s, Cp, 2H), 4.26 (s, Cp, 2H), 4.35 (s, Cp, 2H), 4.76 (s, Cp, 2H), 5.10 (s, Cp, 2H), 7.38–7.50 (m, Ar, 16H), 7.79 (br, Ar, 4H). ^{31}P {^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 45.22. A small amount of the **4c** was used for cyclic voltammetry, but the rest was treated with trimethylsilyl iodide (0.52 mL, 3.6 mmol) in 50 mL of CH_2Cl_2 for 20 min. Water (20 mL) was added and the mixture was stirred for 9 h, then volatile components were removed by vacuum. The red powder (**5c**) was filtered, washed with 6 mL of MeOH and 10 mL of Et_2O, and dried under vacuum (0.80 g, 0.90 mmol, 74% yield with respect to **3**). ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.65 (s, Cp, 2H), 4.22 (s, Cp, 2H), 4.27 (s, Cp, 2H), 4.38 (s, Cp, 2H), 4.82 (s, Cp, 2H), 5.12 (s, Cp, 2H), 7.22–7.50 (m, Ar, 16H), 7.58–7.70 (m, Ar, 4H), 12.49 (s, CO_2H, 1H). ^{31}P {^{1}H} NMR (121.5 MHz, DMSO-d_6): δ 44.93. Anal. Calc. for $C_{40}H_{33}FeIO_2P_2Ru$: C, 53.89; H, 3.73; I, 14.24. Found: C, 53.66; H, 3.76; I, 13.96%.

3.13. ($C_5H_4CO_2H$)Ru(dppf)H (**7c**)

A solution of **5c** (0.30 g, 0.34 mmol) and KOH (0.20 g, 3.6 mmol) in 15 mL of MeOH was refluxed for 18 h. At room temperature, AcOH (0.32 mL, 5.6 mmol) was added in one portion and the mixture was stirred for 20 min. The solvent was reduced by vacuum, 10 mL of water was added, and the yellow solid was filtered and washed with water (3 × 5 mL). The product was dried under vacuum (0.23 g, 0.29 mmol, 87% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ −12.75 (t, Ru*H*, J_{P-H} = 35.4 Hz, 1H), 4.01 (s, Cp, 2H), 4.21 (s, Cp, 4H), 4.25 (s, Cp, 2H), 4.28 (s, Cp, 2H), 4.33 (s, Cp, 2H), 7.28–7.45 (m, Ar, 12H), 7.55 (m, Ar, 4H), 7.65 (m, Ar, 4H), 11.58 (br, CO_2H, 1H). ^{31}P {^{1}H} NMR (161.9 MHz, DMSO-d_6): δ 63.40. Anal. Calc. for $C_{40}H_{34}FeO_2P_2Ru$: C, 62.76; H, 4.48. Found: C, 62.59; H, 4.53%.

3.14. ($C_5H_4CO_2t$-Bu)Ru(dppf)H (**9c**)

A solution of **4c** (0.10 g, 0.12 mmol) and KOH (0.10 g, 1.8 mmol) in 20 mL of MeOH was refluxed for 10 min. At room temperature, the addition of 10 mL of water caused precipitation of the yellow product. The solid was filtered and washed with water (2 × 10 mL). The product was dried under vacuum (70 mg, 0.09 mmol, 73% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ −12.79 (t, Ru*H*, J_{P-H} = 35.1 Hz, 1H), 1.35 (s, *t*-Bu, 9H) 4.00 (s, Cp, 2H), 4.07 (s, Cp, 2H), 4.20 (s, Cp, 2H), 4.26 (s, Cp, 2H), 4.31 (s, Cp, 2H), 4.49 (s, Cp, 2H), 7.20–7.45 (m, Ar, 12H), 7.63 (br, Ar, 4H), 7.77 (br, Ar, 4H). ^{31}P {^{1}H} NMR (121.5 MHz, CD_2Cl_2): AB pattern, δ 62.52 ($\Delta\nu$ = 0.23 ppm, J_{P-P} = 17.1 Hz). FAB$^+$ MS: *m*/*z* 821.1 $[M-1]^+$, *m*/*z* 765.1 $[(C_5H_4CO_2H)Ru(dppf)]^+$.

3.15. pK_a of **7a**

The protonated form (**7a**) has Cp resonances at δ 5.19 and 4.51 in the ^{1}H NMR spectrum in DMSO-d_6. When **7a** was quantitatively deprotonated by DBN (DBN = 1,5-diazabicyclo[4.3.0]non-5-ene) or TMG (TMG = 1,1,3,3-tetramethylguanidine), the Cp resonances shifted to δ 5.08 and 4.27. When **7a** (0.02 mmol) and 1 equiv. of piperidine or pyrrolidine were mixed in 1.0 g DMSO-d_6 and their ^{1}H NMR spectra recorded, the upfield Cp resonance (which is more sensitive) appeared at δ 4.44 (piperidine) and δ 4.41 (pyrrolidine), suggesting that **7a** was 28% deprotonated by piperidine and 40% deprotonated by pyrrolidine. As the pK_a of piperidinium in DMSO is 10.6, the piperidine experiment implies that the pK_a of **7a** is 11.4; as the pK_a of pyrrolidinium in DMSO is 10.8, the pyrrolidine experiment implies that the pK_a of **7a** is 11.2, giving an average of 11.3 for the pK_a of **7a** in DMSO.

3.16. [($C_5H_4CO_2H$)Ru(dppf)H_2][BF_4] (**12**)

In situ preparation from the protonation of **7c** with $HBF_4 \cdot OMe_2$ in CD_2Cl_2. ^{1}H NMR (400 MHz, CD_2Cl_2): δ −7.78 (t, RuH_2, J_{P-H} = 22.2 Hz, 2H), 4.31 (s, dppf Cp, 4H), 4.41 (s, dppf Cp, 4H), 4.83 (apparent t, RuCp, 2H, apparent J = 2.0 Hz), 5.09 (s, RuCp, 2H), 7.60 (m, Ar, 12H), 7.76 (m, Ar, 8H), 8.20 (br, CO_2H, 1H). ^{31}P {^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ 59.17.

T_1 measurements of the dihydride resonance of **12** at 300 MHz in CD_2Cl_2. T_1 = (0.53(2) s, 189.7 K); (0.39(1) s, 198.4 K); (0.318(4) s, 207.8 K); (0.289(5) s, 215.6 K); (0.264(3) s, 224.6 K); (0.259(7) s, 241.6 K); (0.311(7) s, 265.4 K); (0.396(6) s, 282.2 K). Probe temperatures were calibrated with a Wilmad chemical shift thermometer (99.97% methanol + 0.03% HCl) [27].

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