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Ruthenium(II) and Iridium(III) Complexes Bearing Phosphine-Pyridonate and -Quinolinolate Chelates

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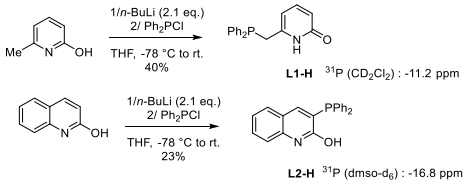
Abstract: Straightforward preparation of five-membered P,N and P,O prochelates were easily achieved from 6-methyl-2-pyridinol and 2-quinolinol. From these ligands, access to the corresponding well-defined ruthenium(II) and iridium(III) was investigated. Owing to the hemilability as well as the reversible proton responsive character of these chelates, the resulting well-defined ruthenium complexes exhibited interesting activities in hydrogenation.

Introduction

Transition metal complexes featuring polydentate donor ligands have found broad applications in homogeneous catalysis and a lot of efforts have been devoted to increase or alter stability/selectivity and activity by steric and electronic ligand modifications.[1,2] Among them, ancillary bidentate diphosphines represent an important part of this class of compounds.[3,4] Owing to the presence of distinct coordination sites, mixed/hybrid ligands represent another part of interesting compounds.[5-8] These prochelates can lead to the formation of stabilized transition metal complexes with unique properties. Depending on the nature of one σ-donor ligand or ligand geometry, partial decoordination can occur expressing hemilabile properties generating a vacant coordination site on the metallic center.[8a] While in all the examples cited above, catalytic transformations occurred at the metal center, ligands containing reactive functionality can cooperate during catalysis to afford multifunctional catalytic systems.[9] Among them, proton responsive/cooperative/non innocent[6f,10-12] and redox active[13,14] ligands represent an important class of ligands of increasing interest.[9-14] One of the most cited examples of bifunctional catalysis involve the use of ruthenium complex containing diphosphine diamine ligands[15] where an acidic proton is held by the ligand through the formation of a N-H functionality[16] and the hydride bound to the ruthenium center allowing the ionic hydrogenation of the carbonyl group through a concerted outer sphere mechanism.
The 2-pyridone/2-hydroxypyridine (Hp) moiety have been at the center of research activities for the preparation of peculiar ligands.[17] 2-Hydroxypyridines can act as carboxylate surrogates but due to the ability of such a functional group to enable hydrogen bonding interaction, 2-pyridone-based ligands have also found broad application for the preparation of water soluble species or self-assembled systems such as the well-known 6-DPPon which has proven efficiency in hydrogenation and related transformations.[18-19] On the other hand, the proximity of the hydroxyl group in 2-hydroxypyridine derivatives can also generate active metal-ligand bifunctional catalytic systems in hydrogen transfer reactions and more interestingly dehydrogenation process.[20-22]
However, to the best of our knowledge nothing is known on the synthesis of phosphinepyridonate derivatives keeping intact the hydroxyl functionality to enable bifunctional catalysis. Therefore, with these reports in mind, we postulate that similar strategy could be used to access corresponding five-membered proton responsive P,O and P,N chelates from 2-pyridone derivatives.
Here we report the synthesis of two new phosphine hybrid ligands featuring 6-methyl-2-pyridinol and 2-quinolinol moieties and the access to the corresponding well-defined ruthenium and iridium complexes. Preliminary investigation in hydrogenation reaction highlights their potential in hydrogen transfer processes.

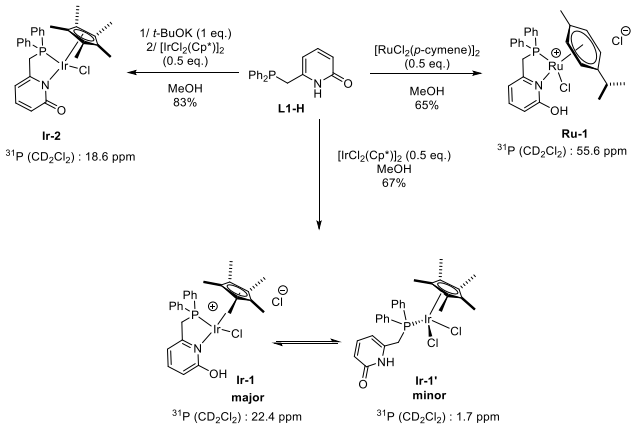
Results and Discussion

The ligands **L1-H** and **L2-H** were directly prepared from 6-methyl-2-pyridinol and 2-quinolinol, respectively. According to a modified procedure of Brunner,[23] reaction of unprotected 6-methyl-2-pyridinol with 2.1 equivalent of *n*-butyl lithium resulted first in the deprotonation of the hydroxyl group followed by the formation of the dianionic species (Scheme 1). Addition of chlorodiphenylphosphine rapidly afforded a complicated mixture of phosphinites and phosphines which, after overnight stirring at room temperature cleanly afforded the crude **L1-Li**. Further treatment followed by protonation with a saturated ammonium chloride solution gave the expected **L1-H** in 40% isolated yield. The preparation of **L2-H** in turn, required the directed *o*-lithiation of 2-quinolinol with *n*-butyl lithium to generate the corresponding *o*-lithiated quinolinolate as key intermediate followed by the addition of Ph_2PCl to afford after treatment and selective protonation of the oxygen atom the ligand **L2-H** in 23% isolated yield.

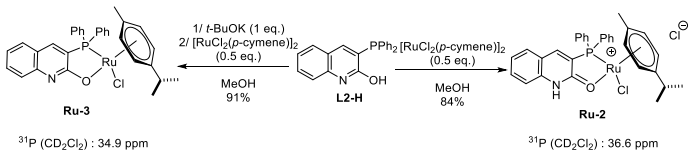


Scheme 1. Preparation of the Phosphine-pyridonate **L1-H** and –quinolinolate **L2-H**.

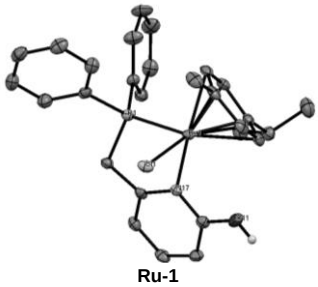
The coordination ability of these ligands to ruthenium and iridium metal centers was explored. We focused our attention on the synthesis of (η^6-arene)ruthenium(II) and three legs piano stool iridium(III) complexes featuring five-membered P,N and P,O chelates. Treatment of the prochelate **L1-H** with $[RuCl_2(p\text{-cymene})]_2$ precursor in methanolic solution ($\alpha = 0.93$)[24] resulted in a red precipitate and afforded the corresponding stable half-sandwich cationic ruthenium(II) complex **Ru-1** (Scheme 2). **Ru-1** formation was monitored by NMR spectroscopy in CD_2Cl_2 (α=0.30) and the spectroscopic data are consistent with the formation of the five-membered chelate. NMR analyses revealed the presence of an acidic proton located at 14.18 ppm and the methylene bridge consists of a set of a doublet of doublet and one triplet located at 4.16 and 3.98 ppm, respectively. Confirmation was obtained in the ^{31}P NMR spectra highlighted by the formation of a sole metallic species with a chemical shift at 55.6 ppm. This result is in line with the known lability of Ru-Cl bond in a polar protic solvent such as methanol and demonstrates that the cationic form is sufficiently stable and did not require the use of stabilizing counteranion.[6e] In contrast to this result, the reaction of $[IrCl_2(Cp^*)]_2$ bearing a bulky pentamethylcyclopentadienyl ligand with **L1-H** in methanolic solution afforded sensitive species in dynamic equilibrium. It is noteworthy that in these cases, a molecule of methanol was observed in a 1:1 ratio MeOH/complex demonstrating hydrogen bonding interactions. Analysis in CD_2Cl_2 revealed the formation of a sole complex **Ir-1** characterized at 22.4 ppm in ^{31}P NMR and ^1H NMR exhibiting the presence of diastereotopic protons on the methylene bridge at 4.27 ($J_{P\text{-}H}$ = 13.7 Hz, $J_{H\text{-}H}$ = 16.5 Hz) and 4.06 ppm ($J_{P\text{-}H}$ = 11.5 Hz, $J_{H\text{-}H}$ = 16.5 Hz). However, slow decoordination of the nitrogen atom leading to the neutral iridium(III) complex **Ir-1'** was observed during these analyses demonstrated by the presence of a new signal in ^{31}P NMR at 1.7 ppm along with the remaining starting complex at 22.4 ppm. Comparison of NMR data with the piano stool iridium complex featuring a 2-(2-diphenylphosphanylethyl)pyridine ligand by Pandey confirmed that reversible chloride displacement occurred accounting on **Ir-1'** complex formation and thus demonstrating the crucial influence of the solvent towards chloride displacement and



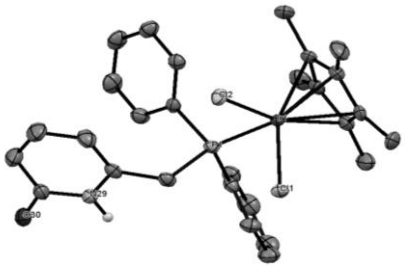
Scheme 3. Reactivity of **L1-H** with ruthenium and iridium metallic precursors.



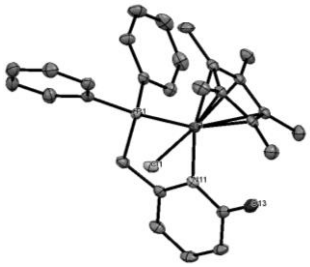
Scheme 3. Neutral and cationic ruthenium(II) complexes featuring **L2**



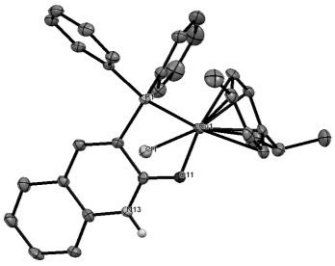
Ru-1



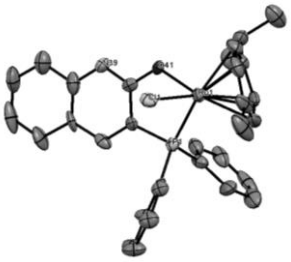
Ir-1'



Ir-2



Ru-2



Ru-3

Figure 1. Thermal ellipsoid (50% probability level) representation of complexes **Ru-1**, **Ir-1'**.CH_2Cl_2, **Ir-2**.CH_2Cl_2, **Ru-2**.2MeOH and **Ru-3**.CH_2Cl_2.

Table 1. Selected bond lengths and bond angles for complexes of Figure 1.[a]

	[M]-Cl	[M]-P	[M]-N/O	C-N	C-O	(N)O-H	P-[M]-N/O	P-[M]-Cl
Ru-1	2.3879(6)	2.2927(6)	2.185(2)	1.353(3)	1.327(2)	0.840	81.1	85.3
Ir-1'	2.409(1)	2.307(1)	-	1.376(5)	1.260(5)	0.881	-	88.7
Ir-2	2.3987(7)	2.2649(7)	2.126(2)	1.398(3)	1.246(3)	-	81.2	89.6
Ru-2	2.3993(6)	2.3125(6)	2.117(2)	1.337(3)	1.262(3)	0.880	80.9	85.3
Ru-3	2.397(2)	2.311(2)	2.075(7)	1.32(1)	1.329(9)	-	81.8	88.0

[a] bond lengths [A] and bond angles [°] of complexes.

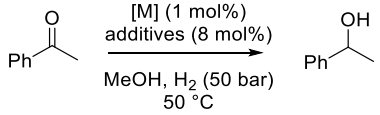
aromatization/dearomatization process.[25] In contrast to these result, prior formation of **L1-K** arising from the deprotonation of **L1-H** with potassium *tert*-butoxide cleanly afford after reaction with $[IrCl_2(Cp^*)]_2$ the neutral piano stool iridium **Ir-2** complex in 83% isolated yield. The formation of five-membered P,O chelate was next investigated starting from **L2-H**. Mixing **L2-H** in the presence of $[RuCl_2(p\text{-cymene})]_2$ metal precursor, clean conversion to the corresponding **Ru-2** complex was obtained in interaction with methanol molecules. In the ^1H NMR spectrum, the supposed O−H signal was shifted downfield at 15.60 ppm in $CDCl_3$ (α = 0.44) with a sharp signal for the methanol whereas in CD_2Cl_2 an upfield signal at 8.50 ppm along with a broad signal at 3.50 ppm for methanol suggested that tautomerization *via* a proton shuttle to N-H occurred.[26] The corresponding neutral ruthenium(II) complex **Ru-3** was

obtained by mixing insitu prepared **L2-K** with $[RuCl_2(p\text{-cymene})]_2$ in 91% isolated yield as a stable complex. Noteworthy that no concentration dependence of the chemical shifts was observed in these complexes.[27]

Finally, formation of complexes **Ru-1**, **Ir-1'.**CH_2Cl_2, **Ir-2.**CH_2Cl_2, **Ru-2.**2(MeOH) and **Ru-3.**CH_2Cl_2 by using solvent diffusion technique (hexane:CH_2Cl_2) was confirmed by X-ray crystallography. ORTEP views at 50% thermal ellipsoids probability are described in Figure 1 and representative bond lengths and angles are outlined in Table 1. In the solid state, hydrogen bonding interactions were observed in the crystal structure of **Ru-1** between the chloride counteranion and the hydroxyl group of the hydroxypyridine ring (OH···Cl = 2.117 Å). In the case of **Ir-1**, only the minor neutral **Ir-1'** selectively crystallized. Interestingly, the crystal structure of **Ir-2** suggests an interaction with the dichloromethane molecule and the oxygen atom of the pyridone ring (O···$HCHCl_2$ = 2.110 Å). The chloride counteranion in **Ru-2** is stabilized by hydrogen bonding with a methanol molecule (Cl^{-}···HOMe = 2.266 Å). The carbonyl moiety presents in complexes **Ir-1'**, **Ir-2** and **Ru-2** is supported by shorter bond lengths of 1.260(5), 1.246(3) and 1.262(3) Å, respectively. In all these structures, the M-Cl bond are comparable with related reported complexes and M-P bonds in the respective complexes are also in the range of the reported values.[25,28]

In light of the potential reversible protonation and hemilability of the chelates in the resulting ruthenium complexes and the crucial influence of solvent, appropriate for the heterolytic

Table 2. Activity of well-defined ruthenium complexes in hydrogenation of acetophenone



Entry[a]	Cat.	Additive	Yield	^{31}P[b]
1	**Ru-1**	None	6%	55.5 (100%)
2	**Ru-1**	DABCO	90%	53.7 (100%)
3	**Ru-2**	None	1%	37.1 (100%)
4	**Ru-2**	DABCO	64%	36.8 (77%) 27.6 (23%)
5	**Ru-3**	None	7%	37.0 (100%)
6	**Ru-3**	DABCO	65%	36.8 (84%) 27.7 (16%)

[a] Reaction were carried out at 50 °C , in 0.5 mL of methanol, acetophenone (0.5 mmol) under 50 bar of H_2 with S/C ratio = 100:1. [b] ^{31}P NMR analysis of the crude reaction mixture after hydrogenation

cleavage of hydrogen, we next examined their reactivity towards acetophenone hydrogenation.[6f,10d,29] The reactions were carried out at 50 °C in methanol under 50 bar of molecular hydrogen with a catalyst/substrate ratio of 1:100. As expected, no or very low activities were detected in the absence of additives (entries 1,3 and 5).[29] Analyses of the reaction mixtures revealed similar ^{31}P displacement as the starting complexes demonstrating that the precatalysts remained intact and the necessity of an external base to ensure the formation of hydride species.[15] Therefore, addition of DABCO as an organic base indicated that these ruthenium complexes could be activated and demonstrated activity in hydrogenation. In the presence of catalytic amount of **Ru-1** along with DABCO, 90% of phenylethanol was formed (entry 2). Analysis after reaction also revealed that the arene remained bound to the ruthenium metallic center and the formation of another species at 53.7 ppm presumably corresponds to the deprotonated neutral ruthenium complex [RuCl(*p*-cymene)**L1**]. To confirm this hypothesis, deprotonated **L1** was reacted with $[RuCl_2(p\text{-cymene})]_2$ (0.5 eq.) to give a brown complex soluble in methanol. Further treatment gave [RuCl(*p*-cymene)**L1**] with a 54.38 ppm chemical shift in ^{31}P NMR($CDCl_3$) with characteristic dearomatized proton patterns in ^{1}H NMR. Addition of small amount of methanol resulted in a slight upfield signal at 54.11 ppm which tend to confirm our assumption.[30] During hydrogenation, no difference of reactivity should be observed between **Ru-2** and **Ru-3**. As results these two complexes exhibited similar activities leading to phenylethanol in 64 and 65%, respectively (entries 4 and 6). From these data, ^{1}H and ^{31}P analyses revealed the side formation of a new complex at 27.6 ppm in ^{31}P NMR. Comparison with reported structures tend to suggest the formation of $[RuCl_2(p\text{-cymene})$**L2-H**] (27.7 ppm) along with [RuCl(*p*-cymene)**L2**] (36.8 ppm), thus demonstrating the partial chelate opening of **L2** during catalysis.[5b,31]

Conclusions

In conclusion, we have reported the preparation of well-defined ruthenium and iridium complexes featuring proton responsive five-membered P,N and P,O chelates. Preliminary evaluation of the ruthenium complexes in hydrogenation of unfunctionalized ketones revealed their promising catalytic activities. Preparation of the corresponding enantiopure ligands is currently underway to evaluate

their activities in enantioselective hydrogenation/reduction of unsaturated substrates with various transition metal complexes as well as dehydrogenation processes.

Experimental

6-((diphenylphosphino)methyl)pyridin-2-ol L1-H

6-methyl-2-pyridinol (1.0 g, 9.16 mmol, 1.0 equiv.) was dissolved in 5.0 mL THF, cooled at 0 °C followed by the slow addition of *n*-BuLi (12 mL, 19.2 mmol, 2.1 equiv.). After one hour stirring, the mixture was cooled to -78 °C, which was added to another solution containing diphenylphosphine chloride (1.6 mL, 9.16 mmol, 1.0 equiv.) in 2.5 mL THF solution at -78 °C. The temperature was allowed to increase naturally to ambient temperature, then the solution was stirred at this temperature overnight. Cloudy orange solution was obtained, which was evaporated, solubilize in acetone/dichloromethane followed by the addition of 20 mL of saturated ammonium chloride solution to precipitate the ligand. Filtration and washings with acetone afforded a white solid as L1-H.

6-((diphenylphosphino)methyl)pyridin-2-ol L1-H (1.06 g, 40%)

^{1}H NMR (400 MHz, CD_2Cl_2): δ 13.00 (brs, 1H, OH), 7.48-7.44 (m, 4H), 7.35-7.33 (m, 6H), 7.25 (dd, 1H, *J*= 9.0, 7.0 Hz), 6.30 (d, 1H, *J*= 9.0 Hz), 5.90 (d, 1H, *J*= 6.8 Hz), 3.37 (s, 2H); ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2): δ -11.23 ; ^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2): δ 165.85 (s), 146.46 (d, J_{P-C} = 9.2 Hz), 141.65 (d, J_{P-C} = 1.5 Hz), 137.46 (d, J_{P-C} = 15.3 Hz), 133.34 (d, J_{P-C} = 19.4 Hz), 129.57 (s), 129.02 (d, J_{P-C} = 6.7 Hz), 117.29 (d, J_{P-C} = 2.2 Hz), 106.49 (d, J_{P-C} = 8.6 Hz), 33.61 (d, J_{P-C} = 19.7 Hz); HRMS-ESI: HRMS-ESI: ($C_{18}H_{16}NONaP$), Calcd: 316.08617; Found: 316.0870 (1 ppm).

3-(diphenylphosphino)quinolin-2-ol L2-H

2-Hydroxyquinoline (1.02 g, 7.00 mmol, 1.0 equiv.) was dissolved in 5.0 mL THF, cooled at 0 °C followed by the slow addition of *n*-BuLi (9.4 mL, 14.70 mmol, 2.1 equiv.) over 10 minutes. The resulting mixture was warmed up to ambient temperature, heated to 50 °C for 10 minutes and then cooled down to room temperature for 20 minutes. Finally the mixture was cooled to -78 °C and was cannulated to a cooled solution of diphenylphosphine chloride (1.2 mL, 6.37 mmol, 0.91 equiv.) in 2.5 mL THF solution at -78 °C. The temperature was allowed to increase naturally to ambient temperature, then the solution was stirred at this temperature overnight. Dark orange to pale brown clear solution was obtained, which was evaporated, quenched with 20 mL degassed water and dissolved with dichloromethane 40 mL, then acidified with 1N HCl until pH was around 3. After separation and extraction, the combined organic layers were dried over $MgSO_4$. Filtration and evaporation afforded a yellow sticky solid. Addition of degassed acetone 30 mL and diethylether 20 mL followed by cooling at -30 °C resulted in the apparition of white precipitates which were collected by filtration. The resulting white solid was further washed with acetone and diethylether to afford L2-H.

3-(diphenylphosphino)quinolin-2-ol L2-H (0.48 g, 23%)

^{1}H NMR (400 MHz, DMSO-d^6): δ 11.94 (d, 1H, *J* = 1.6 Hz), 7.51-7.47 (m, 1H), 7.43-7.41 (m, 7H), 7.34-7.28 (m, 5H), 7.13-7.11 (m, 2H); ^{31}P {^{1}H} NMR (162 MHz, DMSO-d^6): δ -16.80 (s); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d^6): δ 161.91 (d, J_{P-C} = 20.8 Hz, C_{quat}), 143.17 (d, J_{P-C} = 2.1 Hz), 138.91 (s, C_{quat}), 135.4 (d, J_{P-C} = 10.6 Hz, C_{quat}), 133.54 (d, J_{P-C} = 20.5 Hz), 132.57 (d, J_{P-C} = 9.9 Hz, C_{quat}), 130.70 (s), 129.11 (s), 128.78 (d, J_{P-C} = 7.3 Hz), 127.81 (s), 121.94 (s), 118.99 (s, C_{quat}), 115.04 (s); HRMS-ESI: HRMS-ESI: ($C_{21}H_{16}NONaP$), Calcd: 352.08617; Found: 352.0815 (2 ppm)**.**

Acknowledgements

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Keywords: chelate • proton responsive • hydrogenation • ruthenium • iridium

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